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SULFUR MARKETS FOR OHIO UTILITIES

J. F. Foster, et al

Battelle Columbus Laboratories

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16. ABSTRACT

This report discusses possible actions open to Ohio's electric utilities for disposing of sulfur-containing material accumulated as products of the removal of sulfur dioxide from stack gases in a form for reuse as a sulfur-containing by-product. The general objective was to assemble and interpret data on potential sulfur markets which can suggest the form, scope, and direction of the marketing strategy that must be developed by each utility for its own use. The three specific objectives of this study were (1) to identify by-products that could be derived in significant quantities from sulfur dioxide separated form stack gases; (2) to describe and discuss markets that presently exist for these by-products; and (3) to compare by-products sulfur markets developed in other industrial sectors which show approaches to the problem facing the electric utilities. These objectives were fulfilled by this report. By-products in order of importance are sulfuric acid, elemental sulfur, liquid sulfur. Eleven conclusions and recommendations are made. One is that the major outlet for sulfur by-products from all the Ohio utilities probably would be in the Gulf Coast for phosphate fertilizer production. More study is needed to determine at what price the Ohio utilities can compete in this market.

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a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Sulfur	Sulfur dioxide	Ohio	Frasch sulfur
Marketing	Electric utilities	Japan	Local markets
Emissions	Economic analysis	United States	13B
Gypsum	Desulfurization	Sulfur compounds	10A
Regeneration	Ammonium sulfate	Catalytic oxidation	5C
By-products	Stack gases	Gulf coast markets	7A
Sulfuric acid	Air pollution control equipment	Magnesia scrubbing	7B
Fossil fuels		Sulfite-bisulfite scrubbing	7D
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J. F. Foster, D. M. Jenkins,
H. S. Rosenberg and J. H. Oxley

Battelle Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201

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EXECUTIVE SUMMARY

Definition of the Problem

The 27 coal-burning steam-electric plants selected by EPA as the study sample of important plants in Ohio had 92.5 percent of Ohio's total generating capacity in 1970, and consumed 97 percent of the coal burned for electric power generation. Sulfur dioxide emissions from these plants were estimated at 2.4 million tons in 1971. Projected uncontrolled emissions of SO_2 for this group in 1975 will be 3.4 million tons. Although it is doubtful that all these utilities would choose to recover the total emission of sulfur dioxide as salable by-products, these estimates show the large amounts that might be available for marketing.

A variety of processes have been conceived and tested for removing sulfur dioxide from combustion off-gases similar to those emitted by these Ohio utilities. Some processes absorb the sulfur dioxide in a slurry or a solid which has little value and is discarded after use. Other processes are designed to produce salable by-products. This study is concerned with identifying potential markets for such by-products.

The possible by-products include sulfur, sulfuric acid made from recovered sulfur dioxide, pure liquefied sulfur dioxide, calcium sulfate (gypsum), sodium sulfite, and ammonium sulfate. Sulfur can be stored and then converted easily to sulfuric acid to meet variable demand. Sulfuric acid is a basic industrial chemical of wide usefulness but costly to store to meet fluctuating demand and relatively expensive to transport. Liquefied sulfur dioxide has expanding specialty uses in relatively small quantities. Gypsum, sodium sulfite, and ammonium sulfate are solids with limited fields of use in wallboard, paper manufacture, and fertilizer, respectively. All these sulfur-containing materials tend to be in plentiful supply already, although the utility contemplating their recovery has a potential competitive advantage of being able to dispose of them at a price selected to minimize net disposal cost. This selected price may give lower net cost than other disposal routes.

Marketing Experiences from Other Industries

Four industries with experience pertinent to the marketing of sulfur by-products by Ohio utilities are (1) United States utilities with demonstration plants for sulfur removal; (2) Japanese industry, where sulfur has been in short supply in the past; (3) natural gas producers and petroleum refiners, who must remove sulfur from their products; and (4) smelters of metal sulfide ores, with substantial concentrations of sulfur dioxide in their stack gases.

United States Utilities

Present demonstration plants for recovery of sulfur from utility stack gases have used the general approach of marketing sulfur products directly to or through an established chemical company. The vendor of the flue gas desulfurization equipment usually arranges the contacts between the equipment purchaser and the chemical company.

Japanese Industry

The recovery of sulfur by-products has been prompted by the high cost of imported sulfur. The following products have been marketed: sulfur, sodium sulfite, sodium sulfate, sulfuric acid, and gypsum. Now, Japan is in a period of installation of emission controls that augurs a surplus of sulfur. Japanese attempts to alleviate potential surpluses are pointed to production for predictably expanding markets, recovery processes with flexibility to produce more than one product, and an accelerated search for new products or novel uses.

Fossil Fuel Industry

The fossil fuel industries recover a side stream of hydrogen sulfide, which is convertible to sulfur, sulfuric acid, and other products. Thus they have the flexibility to supply several markets. Alternatively,

sulfur can be stored as a stable solid material at minimum cost, and recovered for future sale as markets change. These options are not as available to Ohio utilities, although a tie-in could be arranged to interchange sulfur dioxide from a utility with hydrogen sulfide from a fossil fuel processor to make sulfur. These two gases combine chemically and form elemental sulfur, to be used for further processing, storage, or sale.

Smelters

Smelting companies sometimes use the services of an established chemical company to market the sulfuric acid that is a by-product of their operations. However, the special situation facing Consolidation Mining and Smelting Company (Cominco) of Canada at their plant in Trail, British Columbia, prompted this company to take direct and aggressive action in the development of expanded markets for sulfur products. Cominco sells SO_2 produced at Trail as far away as Glen Falls, New York; Hobbs, New Mexico; and Alaska. Cominco sulfuric acid is marketed mostly on the West Coast of the United States, but a significant amount is transported and sold in Calgary, despite the fact that sulfur recovered from natural gas is available there in tremendous quantities. For many years ammonium sulfate was shipped from Trail to the Orient for use as a fertilizer. Copper Hill in Tennessee currently ships and markets a portion of their production 400 miles or more in jumbo tank cars.

Local Markets for By-Products

The most attractive market for Ohio utilities is obviously those industries within the state itself that consume significant amounts of sulfur or sulfur-containing products.

Sulfur markets in nearby states may be more limited. If sulfur abatement regulations similar to Ohio's are enforced in these neighboring states, any pollution abatement technology feasible for an Ohio utility would also be feasible for competing utilities across the state boundaries. Although sulfur oxide regulations in some adjacent states may enable utility power plants there to use low-sulfur or cleaned coal in place of sulfur dioxide flue-gas cleaning systems, the total amounts of

sulfur that could be recovered in all adjacent states is large compared with the markets currently available for by-product sulfur compounds.

Sulfur or Sulfuric Acid

There appears to be a market in and near Ohio for about 120,000 long tons* of elemental sulfur (269,000 tons* SO_2 equivalent) from Ohio utilities. This market is about 11 percent of estimated 1971 emissions and 8 percent of estimated uncontrolled 1975 emissions from the major Ohio utilities.

Alternatively, there appears to be a market for about 150,000 tons sulfuric acid (98,000 tons SO_2 equivalent) in northern Ohio and up to 150,000 tons acid in southern Ohio. Since sulfuric acid is the major end use of elemental sulfur, production of by-product acid would reduce the sulfur markets estimated in the preceding paragraph. Furthermore, not all acid can be supplied as by-product. Some sulfur-burning capacity for acid manufacture will be needed to provide flexibility. The total potential market in Ohio for utility by-product acid of 300,000 tons would consume about 6 percent of the estimated uncontrolled emissions from Ohio utilities in 1975.

Gypsum

There is a limited potential market in Ohio for by-product gypsum if it is of wallboard quality. The annual market is estimated at about 350,000 tons gypsum (130,000 tons SO_2 equivalent or about 4 percent estimated uncontrolled 1975 emissions). To minimize transportation costs, gypsum would best be recovered at power plants between Toledo and Cleveland.

Fertilizer

Ammonium sulfate is a relatively low-analysis fertilizer. Except when it is specially treated to increase the particle size, it has the

* All quantities of elemental sulfur are given, according to custom, in "long tons" of 2240 pounds. Quantities of other materials are given in conventional "tons" of 2000 pounds, sometimes referred to as short tons.

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additional disadvantage of being hard to handle and apply. Unless Ohio soils become deficient in sulfur, use of ammonium sulfate is unlikely to grow. There are very limited areas of potentially sulfur-deficient soils in Ohio, and widespread sulfur deficiency will probably not be recognized in most of Ohio until at least 5 years after virtual elimination of sulfur emissions from Ohio and Indiana utilities. The markets for ammonium sulfate are expected to remain essentially constant through 1983.

By-product ammonium sulfate supply in and near Ohio appears more than adequate to satisfy consumption. Ohio consumption is estimated at a maximum of 70,000 tons (equivalent to 17,000 tons SO_2). This could be supplied by a single 200 to 250 MW generating station. Considering the large supply of by-product ammonium sulfate already manufactured in and near Ohio, and the limited demand, it appears that ammonium sulfate is not a profitable by-product for sale by most Ohio utilities.

Other Products

The markets for sodium sulfite and liquid sulfur dioxide in and near Ohio are too small to be of significance for disposal of by-product sulfur from Ohio utilities.

New Ventures

One speculative venture, which could provide a significant market for by-product sulfur or sulfuric acid in Ohio would be the establishment of a phosphate fertilizer industry in Ohio. Such a venture, sized to meet Ohio's phosphate fertilizer demand, would consume about 230,000 tons of sulfur dioxide (about 7 percent of estimated 1975 uncontrolled emissions) in the form of sulfuric acid. A phosphate fertilizer operation in Ohio might cause significant water pollution problems. These factors, as well as venture economics, merit more detailed investigations.

Total Local Market

Summarizing, it appears that there is an opportunity to sell up to 12 percent of the sulfur expected to be emitted from Ohio utilities in 1975 in local markets. This sulfur would be sold in the form of elemental sulfur, sulfuric acid, and gypsum. If a phosphate fertilizer industry

were established in Ohio, a new market for sulfuric acid equivalent to about 7 percent of uncontrolled 1975 emissions would be generated. This alternative is highly speculative, however.

By-Product Market Potentials Outside Ohio

One way to market additional sulfur recovered from Ohio utilities would be to ship it to the Gulf Coast. Gulf Coast markets could absorb virtually all sulfur potentially recoverable from Ohio utilities for manufacture of the sulfuric acid that is used there in making phosphate fertilizers. The production of sulfuric acid now depends largely on sulfur mined by the Frasch process, which would be displaced, if the technical and economic feasibility of recovering sulfur from Ohio utilities for sale on the Gulf Coast can be demonstrated.

There are numerous out-of-state utilities that also will be burning high sulfur coal in states between Ohio and Gulf Coast markets. These also might recover by-product sulfur. Their transportation costs would be lower with a consequent competitive advantage for shipments of sulfur in that direction. To examine this competition, a crude estimate was made of the supply and demand for sulfur in selected states closer than Ohio to the Gulf Coast fertilizer manufacturers where the pollution control regulations are expected to require stack gas desulfurization. The results of this analysis indicate that, even if significant amounts of sulfur were recovered by utilities nearer to the Florida and Louisiana markets, there would still be a potential market for sulfur from Ohio utilities. According to this analysis, there is a net estimated surplus of only 230,000 long tons in a market of 4.5 million long tons, assuming 100 percent recovery by all utilities in the selected states exclusive of Ohio. However, many of these out-of-state utilities may adopt throw-away systems instead of systems that recover by-products. In order to penetrate this market, Ohio utilities would have to deliver sulfur on the Gulf Coast at prices competitive with Frasch sulfur.

This analysis has included the production of by-product sulfur recovered at petroleum refineries and from natural gas, plus by-product

smelter acid, but has not assumed any growth in recovery of elemental sulfur from petroleum refineries, any nonacid uses for sulfur, nor any projected growth in sulfur consumption.

New Uses for Sulfur

There are a number of potential new uses for sulfur which are in various stages of development, but none of these have yet reached commercialization and they are not expected to have significant commercial impact before 1985. Although some of these applications may eventually provide outlets for by-product sulfur recovered by the electric utilities, it would be unrealistic to consider such applications in planning emission controls from currently existing power generation stations and plants now under construction.

One of the largest and most promising potential markets for sulfur is in road building. Research at Shell Canada indicates that a mixture of 13.5 percent sulfur, 6 percent asphalt, and 80.5 percent sand can be used as a base course in highway construction, replacing 3 times the thickness of gravel with economic advantage in many areas. It is estimated that the possible Canadian market for sulfur/asphalt road building materials could require more than 600,000 long tons of sulfur annually. Shell Canada is actively trying to develop markets for sulfur in road construction.

Another potential use for sulfur is in the manufacture of rigid foams which would have application as insulation in construction and possibly in subsoil in Arctic areas. Technology has been developed for producing rigid sulfur foams with densities ranging from 7 to 30 pounds per cubic foot. The annual Canadian market potential for sulfur in this application has been estimated to be about 300,000 long tons.

A third possible application may be sulfur-concrete mixtures. Sulfur-concrete is expected to find use initially in precast products, concrete pipes, ground anchors, street curbs, traffic barriers, etc.

Other possible uses for sulfur which may have commercial significance include use in traffic paints; use as an impregnant for porous materials like concrete, ceramics, and wood; use in a new granulated form of gypsum as a soil conditioner, as a reinforcing agent for polymers, and for incorporation into the polymer molecules themselves.

Suggested Marketing Methods for Utilities

At present the most expedient course of action for many Ohio utilities may be to seek a marketing agreement with a company already having the necessary distribution system and marketing expertise, rather than to build immediately for themselves the necessary expertise to market chemical by-products. By virtue of their sulfuric acid operations in and near Ohio, obvious candidates for marketing by-product acid from Ohio utilities include Allied Chemical and Du Pont. For marketing elemental sulfur, not only these companies but also other acid manufacturers and sulfur producers such as Texasgulf and Freeport Minerals could be considered. Other producers should be considered for marketing of the other possible by-products.

However, those utilities that are capable of assuming a more active role in marketing, in the face of a projected sulfur surplus, are more likely to preempt the markets that are potentially available. For instance, a substantial part of the uncontrolled emissions of SO_2 from all Ohio utilities probably could be sold if all the recognizable local and Gulf Coast markets for sulfuric acid, sulfur, and fertilizer were aggressively pursued.

Finally, a more active research and development effort in the search for new products utilizing sulfur should be considered by the larger utilities or cooperatively on a group basis.

The developments at the Trail smelter of Cominco over the past 50 years are an example of the success possible with a dedicated company effort.

TOPICAL REPORT

on

SULFUR MARKETS FOR OHIO UTILITIES

to

STRATEGIES AND AIR STANDARDS DIVISION
OFFICE OF AIR AND WATER PROGRAMS
ENVIRONMENTAL PROTECTION AGENCY

September 25, 1973

by

J. F. Foster, D. M. Jenkins, H. S. Rosenberg,
and J. H. Oxley

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INTRODUCTION

The Strategies and Air Standards Division of the Environmental Protection Agency Office of Air and Water Programs is sponsoring a series of concurrent studies to generate technical information needed by State agencies to develop power plant control strategies which are consistent with EPA's clean fuels policy. Not only must Federal regulations on new plants be met, but there are also State regulations on new and old plants to be considered, and, as shown in Table 1, these vary from state to state.

This Battelle report discusses possible actions open to Ohio's electric utilities for disposing of sulfur-containing materials accumulated as products of the removal of sulfur dioxide from stack gases in a form for reuse as a sulfur-containing by-product. Two options not considered here, but treated in other studies, are (1) to burn low-sulfur

TABLE 1. SUMMARY OF 1975 RESTRICTIONS ON SULFUR EMISSIONS FROM LARGE STEAM-GENERATION PLANTS IN SELECTED REGIONS

State	1970 Fossil Fuel Use[a] (10^{12} Btu) Coal	Oil	Gas	1975 Sulfur Emission Restrictions[b]	Remarks
Georgia	178.1	9.5	59.4	3.0% S	Approved. New sources 0.8 lb SO_2/MM Btu oil; 1.2 coal.
West Virginia	348.8	0.7	0.4		Approved. Priority I Regions: Weirton-Wheeling; Cumberland. Priority II: Parkersburg. Priority III: all other. Fuel restrictions are recommendations, not regulations.
Kanawha Valley				1.6 lb SO_2/MM Btu	
Priority I & II				2.7 lb SO_2/MM Btu	
Priority III				3.2 lb SO_2/MM Btu	
				1.5% S oil	
				2.0% S coal	
Ohio	794.6	4.1	13.9		Approved. All regions must meet Priority I levels by July 1, 1978. Priority I Regions: Cincinnati[c], Cleveland; Marietta[c]; Northwest Ohio; Steubenville; Toledo; Youngstown[c]; Zanesville.
Priority I				1.0 lb SO_2/MM Btu	
Priority II				1.6 lb SO_2/MM Btu	Priority II: Dayton; Mansfield-Marion.
Priority III				3.1 lb SO_2/MM Btu	Priority III: Columbus; Portsmouth-Ironton; Sandusky; Wilmington-Chillicothe-Logan.
Kentucky	396.9	0.6	8.6		Approved. Priority I Region is Louisville and was granted an extension to July 1977 to enforce population and meet standards. Priority II: Evansville; Paducah; Cincinnati. All but Cincinnati given until July 1978 to meet secondary standard. All other regions are Priority III.
Priority I (Louisville)				1.2 lb SO_2/MM Btu coal	
				0.8 lb SO_2/MM Btu oil	
Priority II				2.0 lb SO_2/MM Btu coal	
				1.5 lb SO_2/MM Btu oil	
Priority III				3.5 lb/MM Btu coal	
				2.0 lb SO_2/MM Btu oil	

(a) Fossil fuel consumed only by steam-electric plants. Does not include residential, commercial, or industrial consumption.

(b) These restrictions are indicated on the basis of information presently available to Battelle-Columbus. However, some of them might be changed between now and 1975.

(c) Classified Priority II by EPA, I by Ohio.

synthetic or natural fuels, or (2) to absorb sulfur dioxide from stack gases into a throw-away product.

The general objective of the Battelle assignment was to assemble and interpret data on potential sulfur markets which can suggest the form, scope, and direction of the marketing strategy that must be developed by each utility for its own use.

The three specific objectives of this study were (1) to identify by-products that could be derived in significant quantities from sulfur dioxide separated from stack gases; (2) to describe and discuss markets that presently exist for these by-products; and (3) to compare by-product sulfur markets developed in other industrial sectors which show approaches to the problems facing the electric utilities.

The sulfur-containing by-products considered attractive economically and potentially recoverable from utility stack gases in order of importance are sulfuric acid, elemental sulfur, liquid sulfur dioxide, calcium sulfate, ammonium sulfate, and sodium sulfite.

The industrial classifications of by-product sulfur producers with experience pertinent to utility problems, as selected for this study, are (1) the American electric utilities with demonstration sulfur-removal facilities installed or planned; (2) Japanese industries, including some electric power plants with sulfur emission controls; (3) the fossil-fuel industries of United States and Canada, including production of natural gas, petroleum refining, and coke production; (4) the smelting industry processing sulfur-containing ores of copper, lead, and zinc.

The information collected concerning these industries is considered in terms of its application to the particular group of 27 coal-burning steam-electric generating plants of Ohio utilities selected by EPA as the representative sample of important plants in Ohio.

This study does not consider any individual power plant of the Ohio group as to its own available or projected markets and marketing strategy. However, the general conclusions are made as specific as possible, so that they may be applied by the individual utilities while developing their unique plans for action.

It may be for a particular utility that by-product sulfur recovery and sale either is not practical or is not a preferred option.

Nevertheless, this report is intended to provide a basis for a preliminary appraisal of options, as well as background information to guide more detailed studies that should be developed before a final decision is reached.

REVIEW OF THE TECHNOLOGICAL SITUATION

Sulfur Emissions from Ohio Utilities

Twenty-seven major utility power plants that are responsible for about 61 percent of coal-fired utility SO_2 emissions in the Air Quality Control Regions of Ohio (ACQR) grouped by power system are listed in Table 2. A code number has been assigned to each plant for reference in the following discussion. The name-plate generating capacity in 1970 and the coal used with its percentage of sulfur in 1970 are also given for reference. More recent data are used below for 1971 emission calculations. The planned capacity increase listed for each plant in the period between 1971 and 1975 is also used as given to calculate the increment in emissions by 1975.

An estimate of total emissions of sulfur dioxide from the electric power plants in each Air Quality Control Region wholly or partially within the State of Ohio is presented in Table 3. The totals in Column 4 of the table include one or two nonutility power plants with significant amounts of emissions, power plants outside of Ohio but within the interstate regions, and several municipal plants with significant emissions. The fifth column shows a subtotal by region of the emissions from those of the 27 selected plants within each region. To the right of each subtotal are shown the calculated emissions from each of the 27 plants identified by code number. Finally, at the extreme right are given the calculated plant increases in emission until 1975 with the amount for individual plants identified by code number. Thus, these data show that about 4 million tons of sulfur dioxide are emitted in the Ohio AQCR's of which about 2-1/2 million tons was emitted in 1971 by the 27 plants under consideration. The estimates of the planned increases until 1975 add

TABLE 2. SELECTED GROUP OF MAJOR COAL-BURNING POWER PLANTS IN OHIO

System	Code No.	Power Plant	Nameplate Capacity 1970, mW	Planned Capacity Increase, mW (year)	Location AQCR No.	Location Priority (SO_2)	Location County	1970 Coal Use (10^3 tons)	Average Percent Sulfur
Cincinnati Gas & Electric Company	1	W. C. Beckjord # 1-6	1,221.3	500-(75)	79	II (a)	Clermont	3,038	2.81
	2	Miami Fort	519.2	500-(75)	79	II (a)	Clermont	969	3.71
Cleveland Electric Illuminating Co.	3	Ashtabula	456.0		178	II (a)	Ashtabula	942	4.24
	4	Avon Lake	1,275.0		174	I	Lorain	1,977	2.66
	5	Eastlake	577.0	680-(72)	174	I	Lake	1,780	2.30
	6	Lake Shore	514.0		174	I	Cuyahoga	1,271	2.61
Columbus & Southern Ohio Elec. Co.	7	Conesville	433.5	842-(73)	183	IA	Coshocton	1,303	4.63
	8	Picway	230.8		176	III (b)	Pickaway	381	3.35
	9	Poston	232.0		179	II (a)	Athens	732	2.01
	10	Walnut	75.0		176	III (b)	Franklin	129	3.11
Dayton Power & Light Company	11	O. H. Hutchings	414.0		173	II (b)	Montgomery	897	1.21
	12	F. M. Tait	444.1		173	II (b)	Montgomery	1,010	1.57
	13	J. M. Stuart	610.2	1830(71-74)	103	III (b)	Brown	348	2.23
Ohio Edison Company	14	R. E. Burger	544.0		181	I	Belmont	1,276	3.67
	15	Edgewater	192.9		174	I	Lorain	311	2.63
	16	Gorge	87.5		174	I	Summit	211	3.42
	17	Niles	250.0		178	II (a)	Trumbull	557	3.34
	18	W. H. Sammis	1,680.5	623-71	181	I	Jefferson	3,863	2.64
	19	Toronto	315.8		181	I	Jefferson	410	2.39
Ohio Power Company	20	Cardinal	1,180.0		181	I	Jefferson	3,020	2.98
	21	Muskingum	1,466.8		179	II (a)	Morgan	3,683	5.02
	22	Philo	500.0		183	IA	Muskingum	984	3.32
	23	Tidd	222.2		181	I	Jefferson	581	2.94
	24	Gavin	--	1300-74	103	III (b)	Gallia		
Ohio Valley Electric Corp.	25	Kyger Creek	1,086.3		103	III (b)	Gallia	2,803	4.26
Toledo Edison Co.	26	Acme	337.0		124	I	Lucas	350	2.45
	27	Bay Shore	639.5		124	I	Lucas	1,480	2.22
Total			15,504.6(c)					34,306(c)	

(a) Sulfur emissions below primary ambient air quality standard. Federal Register Vol. 37, No. 145, Thursday, July 27, 1972.
(b) Sulfur emissions below secondary ambient air quality standard. Federal Register Vol. 37, No. 145, Thursday, July 27, 1972.
(c) Equivalent to 92.5% of total generating capacity and 97% of total coal used in Ohio for electric power generation.

TABLE 2. UNCONTROLLED SULFUR DIOXIDE EMISSIONS FROM SELECTED GROUP OF OHIO POWER PLANTS IN 1971(a,b)
(1000 T/yr)

Air-Quality Control Region			Total Regional Coal-Fired Utility Emissions	Total in Each AQCR From 27 Selected Utilities	Emissions From Individual Plants, Code No.(b) - Amount	Planned Increases(d) Until 1975, Code No.(b) - Amount
No.	Name	SO_2 Priority				
079	Cincinnati	II	437	334	#1-171;#2-163	+ #2-156
103	Huntington WV	III(c)	378	254	#13-15;#24-0;#25-239	+ #24-70, #13-45
124	Toledo	I	591	81	#26-19;#27-62	
173	Dayton	II	59	50	#11-20;#12-30	
174	Cleveland	I	464	433	#4-143;#5-200;#6-71; #15-19;(#16-16)(e)	+ #5-235
176	Columbus	III(c)	29	29	#8-21;#10-8	
177	NW Ohio	I	3	0	None	
178	NW Pa - Youngstown	II	310	95	#3-61;#17-34	
179	Parkersburg-Marietta	II	474	415	#9-25;#21-390	
181	Steubenville	I	823	478	#14-83;#18-199;#19-21; #20-142;#23-33	+ #18-74
183	Zanesville	IA	388	388	#7-317;#22-71	+ #7-616
Totals 1971			4006	2427		961
Totals 1975			4967	3386		

(a) Derived from "Input data by regions for power plant analysis": Appendix C of Draft Reports for each AQCR "Modeling Analysis of Power Plants for Compliance Extensions. -- AQCR." Walden Research Corp., for Source Receptor Analysis Branch, Monitoring and Data Analysis Division, of OAQPS, OAWD, EPA. Various dates, 1973.
(b) See Table B-2.
(c) Priority III Regions calculated from coal consumption and average sulfur in coal.
(d) Estimated from nameplate capacity.
(e) No by-product recovery is planned for Plant #16, which will be discontinued in 1981.

almost another million tons to give a total for all Ohio regions of about 5 million tons of SO_2 emissions. It appears that these totals represent emissions that will potentially be a source of sulfur by-products from Ohio competing for appropriate markets or disposal procedures within and outside the state boundaries.

The calculated amounts of emissions for individual power plants in Priorities I and II in 1971 were from EPA excerpts of reports labeled "Input Data AQCR Power Plant Analysis" provided by the EPA Project Monitor. The emissions for Priority III regions were calculated from plant fuel consumption and sulfur content data for 1971 reported on Federal Power Comaission Form 67 by assuming that 95 percent of sulfur in the coal appears as sulfur dioxide in the flue gases.

The estimates of emissions from new units to be placed in service were calculated as the ratio of the name-plate capacities of the new and old units in the same plant times the 1971 annual SO_2 emission of the old plant. Finally, the estimated emissions for the new Gavin Plant (No. 24) were derived as a ratio of its name-plate capacity to name-plate capacity of Kyger Creek Plant (No. 25) in the same region and same county, assuming equal efficiency of coal consumption and 1 percent sulfur in the coal, which was based on an estimate received from EPA.

Properties of By-Products

The Ohio plants to which these studies are directed will be burning high-sulfur coal while discharging the gases from the combustion process into the furnace stack and then into the atmosphere. Almost all the sulfur content of these gases is gaseous sulfur dioxide (SO_2), plus a much smaller amount of sulfur trioxide (SO_3). These two products are formed from over 90 percent of the original sulfur in the coal, and the remaining sulfur stays in the coal ash. To stay within permissible limits a major part (generally above 85 percent for Ohio coals) of the gaseous SO_2 must be separated from the combustion gases and discarded in an acceptable form or converted to by-products with useful properties.

Sulfur Dioxide

Sulfur dioxide is the predominant by-product from which all others are derived. It is sold also as a primary by-product for use as a preservative and bleach in foods, for solvent refining of lubricating oils, for preparation and bleaching of sulfite pulp and paper stock, for conversion to sulfur trioxide, and as a disinfectant and fumigant.

It is a gas which is easily liquefied for storage or shipment under a pressure of about 35 psig at room temperature. As a dry liquid it is noncorrosive to steel pressure containers. The gas is easily soluble in water or dilute acid to form an unstable solution of sulfurous acid, which can be decomposed by heating to drive off sulfur dioxide gas from the solution.

Sulfuric Acid

Sulfur dioxide is oxidized by air in the presence of a catalyst to form sulfur trioxide (SO_3), which combines spontaneously and irreversibly with water vapor to form sulfuric acid. With carefully controlled conditions of temperature, flow rate, and composition of the reacting mixture, 97 percent of the input of sulfur dioxide can be converted in a one-pass sulfuric acid plant. Starting with pure SO_2 and pure dry air, sulfur acid of high purity can be produced from the SO_3. A range of high acid concentrations to serve any market is available. The usual practice is to absorb the SO_3 in 100 percent sulfuric acid and then dilute this solution back to 100 percent acid with water.

Pure concentrated sulfuric acid cannot always be made from by-product sulfur dioxide in stack gases because of possible economic limitations on the removal of fly ash and water vapor completely from feed to the by-products acid plant. Traces of metals and carbon from small amounts of the dark-colored ash may be carried into the acid, which then cannot meet purity and color specifications for some applications. Water vapor formed as a combustion product may dilute the acid to a concentration less than the usual commercial grades having nearly 100 percent acid. The process to be used by a utility in producing sulfuric acid should

therefore be examined to be sure its product satisfies the intended market.

Elemental Sulfur

Sulfur dioxide reacts with reducing agents with loss of its oxygen and formation of elemental sulfur under appropriate reaction conditions. The common reducing agents contain carbon, hydrogen, or both. They include natural gas (methane), carbon monoxide, coke, hydrogen gas, and hydrogen sulfide. Any of these might be used by a utility to convert recovered SO_2. The choice would ultimately fall on the reducing agent which imposed the lowest processing cost. Hydrogen sulfide and natural gas are the only reductants which have been used on a large commercial scale. Coke also has been used commercially with satisfactory results.

Elemental sulfur has properties which make it easy to handle and store. It is an inert solid that does not deteriorate in open storage. It can be prepared in high purity. It is used in the rubber industry and as a fungicide. The largest use is for conversion to sulfur dioxide for manufacture of sulfuric acid.

Sulfur-Containing Solids

Various solid materials can be prepared as by-products of sulfur recovery or as intermediates for further treatment. Solids may be desirable because they can be separated from the water portion of the wash liquid by centrifuging or filtration as part of the recovery process. The particular solid material depends upon the material used in the process as an absorbent to react with the sulfur dioxide in the flue gas.

Each individual absorbent gives a different solid by-product or intermediate, but all have the common property of being an alkali to neutralize the acid solution of sulfur dioxide. Thus, the reacting alkalies may be calcium-containing limestone, lime, or slaked lime, all of which produce calcium sulfite or calcium sulfate as the solid by-product, or other calcium-free alkaline materials including ammonia, sodium hydroxide and soda ash, and magnesia. Each of these reactants can produce one or more useful solid by-products, or intermediate products that are processed further to regenerate sulfur dioxide and recover the

original alkali absorbent. The calcium sulfite and calcium sulfate products obtained by absorption with lime have received much attention, because the low cost of the absorbents should be reflected in relatively low cost by-products. Calcium sulfate from mined deposits is used in plaster board for wall construction. Calcium sulfate also might find some use as a soil conditioner, or it may be a throw-away product used for land-fill. Calcium sulfite can be oxidized to calcium sulfate, or it may have some use as a filler in plastic materials. The other solids formed from absorbents ammonia, magnesia, or sodium hydroxide are intermediates which are regenerated to recover the relatively costly absorbent plus sulfur dioxide, so that the absorbent can be reused, and the sulfur dioxide can be converted to sulfuric acid.

These examples indicate the large variety of processes which have been investigated for sulfur dioxide removal from flue gases, and emphasize the number of by-products that are possible. The variety of available processes and diverse nature of the by-products imposes the necessity for a difficult decision by each Ohio utility to select as far as possible a process that will be suited to its own needs at minimum cost.

Sulfur Dioxide Recovery Processes Under Development

Process Requirements and Capabilities

The optimum SO_2 recovery process for utilities would give adequate emission control without significantly increasing the cost of electric power, negligible cooling of the stack gas to avoid loss of plume buoyancy, and an easily storable and concentrated product with a stable and attractive market. However, generally there must be some economic trade-offs between process costs and by-product income (or disposal costs). Proposed processes can produce either elemental sulfur, sulfuric acid, liquid SO_2, ammonium sulfate (a fertilizer material), calcium sulfate (gypsum), or sodium sulfite or sulfate. Some are limited to one product, others make two, and in some the product type is optional. Most of the SO_2 recovery processes now under commercial development in the United States produce either sulfur or sulfuric acid. The recovered SO_2 can then be converted to sulfur or other sulfur-containing

products. These SO_2 recovery processes include magnesia scrubbing, sulfite scrubbing with thermal or electrolytic regeneration, and catalytic oxidation.

Demonstration Plants for SO_2 Removal

The EPA has given financial assistance to build and operate demonstration plants for four processes at steam-electric plants. These are (1) the Chemico/Basic magnesia scrubbing process now in operation on an oil-fired boiler at Boston Edison's Mystic Station and scheduled for demonstration on a coal-fired boiler at Potomac Electric Power's Dickerson station. (2) the Davy Powergas/Allied Chemical sulfite scrubbing process with thermal regeneration at Northern Indiana Public Service Company's Mitchell Station; (3) the sulfite scrubbing process with electrolytic regeneration at a Wisconsin Electric power station in Milwaukee; and (4) the Monsanto catalytic oxidation process at Illinois Power's Wood River station. The magnesia scrubbing and catalytic oxidation installations at Mystic station and Wood River station have been completed, but no significant operating experiences have been obtained up to the date of this report. The two sulfite scrubbing installations are scheduled to start up in 1974. In addition, Philadelphia Electric is installing a privately funded magnesia scrubbing process at its Eddystone plant.

Characteristics of Processes in the Demonstration Plants

The first three SO_2 recovery processes discussed above wash the flue gas with a water slurry or solution which cools it to about 125 F. This is too low a temperature to leave the cleaned gas with enough buoyancy to rise properly through the stack, so that some reheating is required. The fourth process, catalytic oxidation, requires heating of the flue gas above the normal discharge temperature from existing plants. It must be preheated to about 850 F before it contacts the catalyst for the oxidation reaction to occur.

Magnesia Scrubbing. Thus far, the only commercial-sized installation of magnesia scrubbing in the United States is on the oil-fired boiler at Mystic Station; another installation on a coal-fired boiler of Potomac Electric Power Company is scheduled to go on stream in 1974. For operation on flue gas from the coal-fired boiler (refer to Figure 1), the gas is first sent to a particulate scrubber for efficient removal of fly ash. The flue gas is then washed with fresh magnesia (MgO) slurry in an absorber to form magnesium sulfite ($MgSO_3$) and some magnesium sulfate ($MgSO_4$), which are centrifuged, dried, and heated (calcined) to recover MgO and SO_2. The MgO is returned to the absorber and the SO_2 is used to make high-quality sulfuric acid. The cleaned flue gas is reheated and sent up the stack. The process advantages are minimal solid waste disposal problems, no water pollution, and a potential credit from the sale of sulfuric acid. However, the process is susceptible to problems from fly ash and sulfate buildup in the system which may have to be purged, and possible reduction of capacity for absorption of SO_2 by the recycled MgO.

Sulfite-Bisulfite Scrubbing with Thermal Regeneration. Five commercial installations of the sulfite-bisulfite scrubbing process are already operating in the United States and Japan. In addition, the Davy Powergas Company will install the first full-scale demonstration plant project to treat the stack gas from a coal-fired boiler at the Mitchell Station of Northern Indiana Public Service Company. The end product of this plant will be elemental sulfur which will be produced in a second step by direct reduction of the recovered SO_2 with natural gas, using the Allied Chemical process.

The flue gas passes through (1) a prescrubber where it is humidified, (2) then through an absorber where SO_2 is removed with sodium sulfite solution, (3) the clean stack gas is reheated and sent to the stack (refer to Figure 2). The scrubbing solution is regenerated by evaporation of water and SO_2 in a crystallizer which precipitates sodium sulfite solids. The vapor product is cooled to condense out all of the water. The pure SO_2 gas can be further processed to liquid SO_2, sulfur, or sulfuric acid. Condensed water is used to redissolve the sulfite solids for recycle through the scrubber. Sulfate formed in the scrubber cannot be regenerated and is removed from the system by discarding part

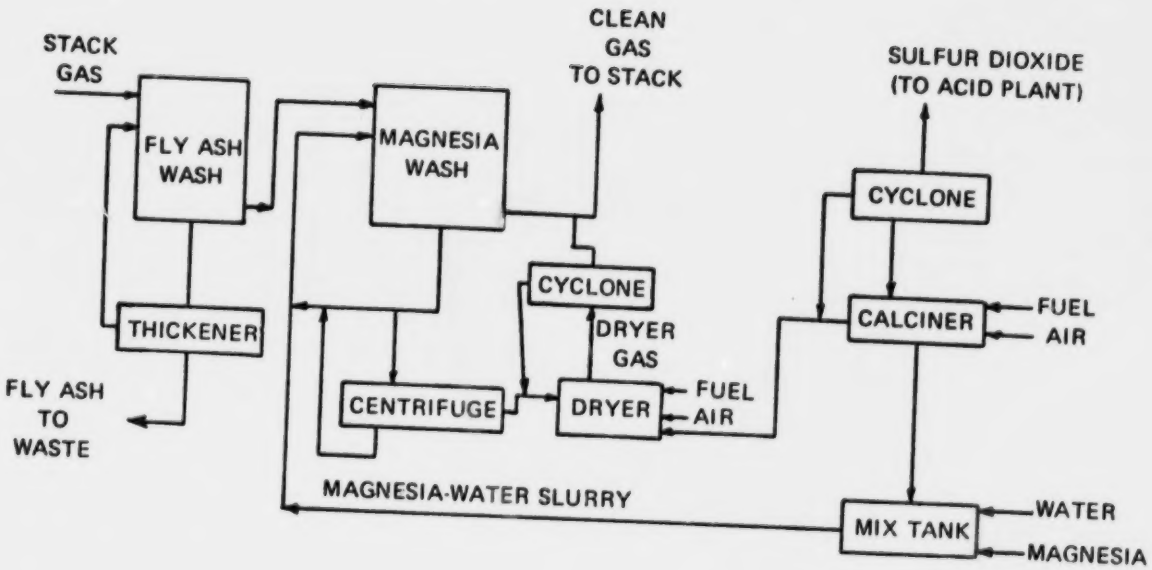

FIGURE 1. MAGNESIA SCRUBBING WITH SULFUR DIOXIDE RECOVERY

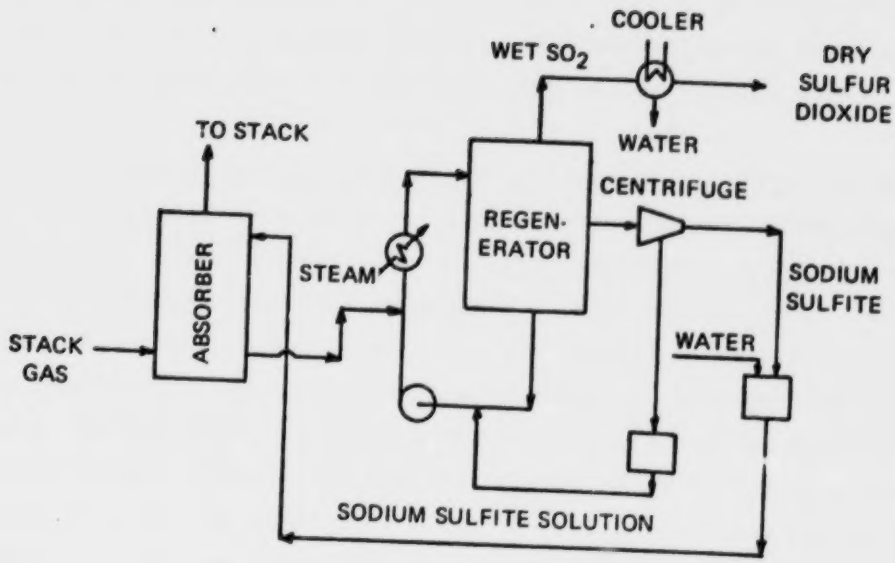

FIGURE 2. SULFITE-BISULFITE ABSORPTION OF SULFUR DIOXIDE WITH THERMAL REGENERATION

of the scrubbing solution continuously or by selective crystallization and removal of solid sodium sulfate. The discarded solution must be treated to eliminate polluting effects of chemical oxygen demand on groundwaters due to its sulfite content.

The specific advantage of the process is the simplicity of its unit operations. The main disadvantage is its sensitivity to buildup of contaminants (sodium sulfate, sodium thiosulfate, sodium polythionates, and a small amount of elemental sulfur), thus necessitating discarding some of the solution with the loss of sodium content, which must be replenished.

Sulfite-Bisulfite Scrubbing with Electrolytic Regeneration. Stone & Webster/Ionics are developing an alternative method for regenerating spent absorber solution from sulfite-bisulfite scrubbing. A pilot-scale demonstration of this process on a 70-mw coal-fired boiler in Milwaukee is being funded by the EPA. This process is very similar to the one described above except for the treatment of the spent absorber solution. In the process (refer to Figure 3) there are two recirculating absorption stages. Alkali solution is introduced in the upper stage where it reacts with SO_2 and makes sodium sulfite. This solution passes from the upper stage to the lower stage, during which a sizeable amount of the sulfite is converted to sodium bisulfite by further absorption of SO_2. Side reactions convert some of the sulfite and bisulfite to sulfates. The final solution containing the sulfite and bisulfite is reacted with dilute sulfuric acid to free SO_2 and also form sodium sulfate. The SO_2 is stripped from solution, dried, and processed to liquid SO_2, sulfur, or concentrated sulfuric acid.

The sodium sulfate solution is pumped into an electrolytic cell, which simultaneously generates alkali for recycling to the absorber and acid for freeing the SO_2 from the sulfite-bisulfite solution. Sulfate formed as a side reaction by oxidation is rejected from a special cell configuration as pure dilute H_2SO_4, without the loss of sodium ion.

This process requires a considerable amount of power to operate the electrolytic cells so that it is most applicable to plants having suitable amounts as off-peak loads. Although the process avoids

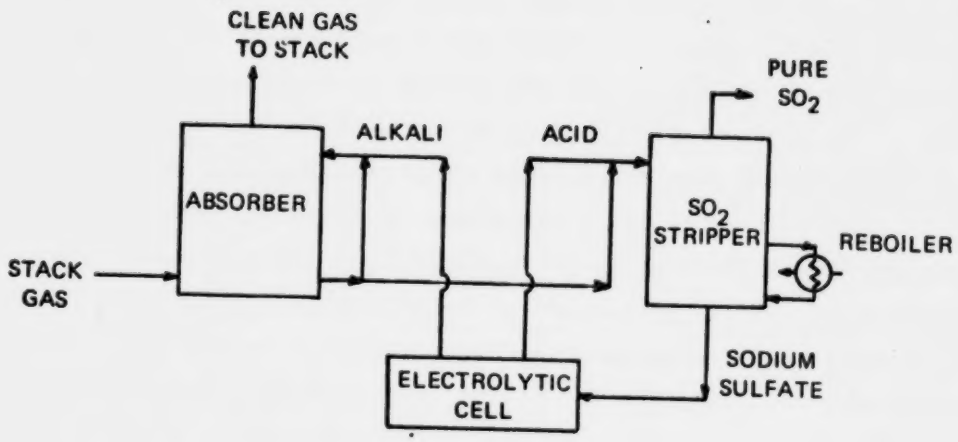

FIGURE 3. SULFITE-BISULFITE SCRUBBING WITH ELECTROLYTIC REGENERATION

the loss of sodium ion by producing dilute H_2SO_4 from the sulfate formed in the absorber, this dilute acid must either be sold or neutralized with limestone for waste disposal.

Catalytic Oxidation. Small pilot plant demonstrations of the catalytic oxidation process were tried in 1963 at the Seward, Pennsylvania, plant of Pennsylvania Electric Company and in 1968 at the Portland, Pennsylvania, plant of Metropolitan Edison Company. The first commercially sized installation of the Monsanto Cat-Ox process was placed in operation in September, 1972, on a coal-fired 100-mw unit of Illinois Power Company at Wood River. The system (refer to Figure 4) uses a fixed-bed catalytic converter to oxidize the SO_2 in the gas stream to SO_3 which can be collected at about 78 percent H_2SO_4.

The flue gas must be at about 850 F upon entering the converter, so that reheat is necessary for retrofit installations. Reheat is accomplished by the combustion of an auxiliary fuel, but energy requirements are minimized by recovering the heat from the treated flue gas in a regenerative heat exchanger. Because of leakage across the heat exchanger, the SO_2 removal efficiency is less than the total percentage conversion of SO_2 to SO_3. The SO_3 is scrubbed from the flue gas with H_2SO_4 in a packed bed absorbing tower and acid mist is removed in a highly efficient fiber collector.

The flue gas must be relatively free of fly ash before entering the converter in order to avoid fouling the catalyst. Provision is made for cleaning the catalyst on a vibrating screen, but some of the catalyst is lost in each cleaning and the required frequency of cleaning has not yet been established. The Wood River installation was operated for only a few days before it became apparent that the catalyst and mist eliminator had to be protected against fouling while the reheat burners were being readjusted. A revision of the reheat system is currently under way. The main advantage of this process is simplicity; no operating labor or raw materials are theoretically required and it is hoped no regeneration step is necessary.

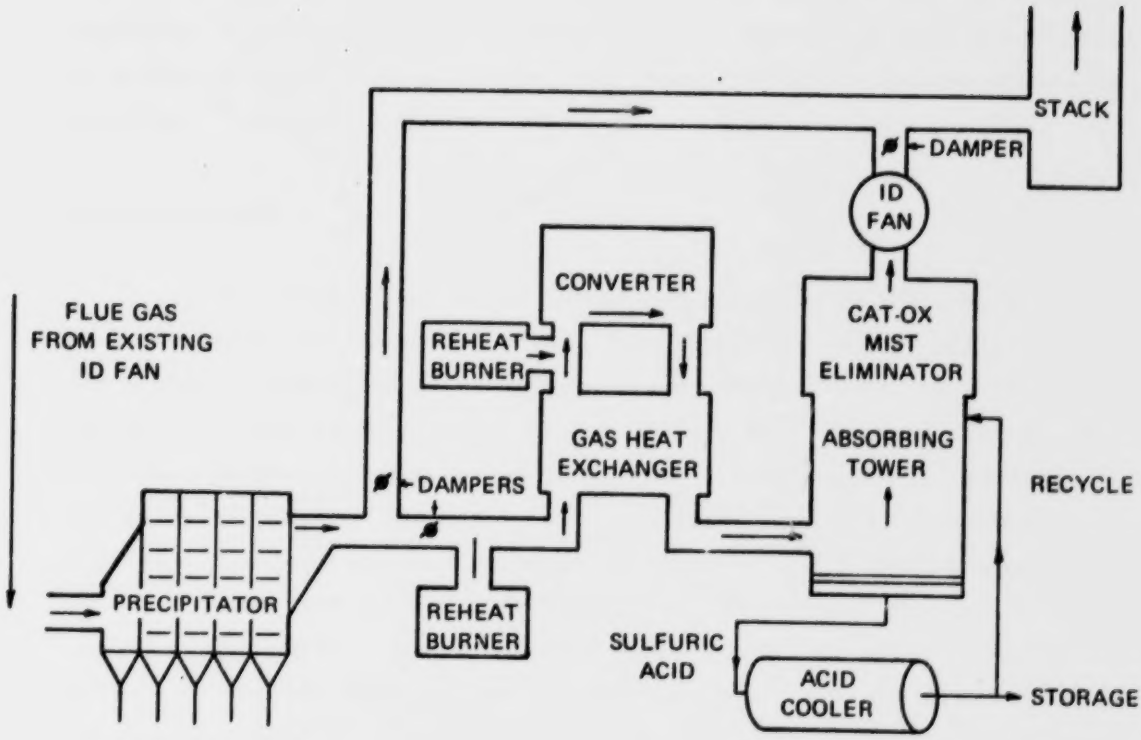

FIGURE 4. CATALYTIC OXIDATION (RETROFIT CASE)

The 78 percent sulfuric acid produced by The Monsanto Cat-Ox process is more dilute than the 93-98 percent acid usually sold in commerce, but it is suitable for many applications. Shipping costs per unit of acid are higher, however. In addition, the acid may be discolored by fly ash and may contain traces of dissolved metallic impurities from the fly ash. It is not suitable for uses that require high purity, such as battery acid, manufacture of detergents for food processing, and sulfonated additives for lubricants. It can be used for fertilizer manufacture and in pickling steel to remove scale, and these two uses represent the major portions of the acid market.

Estimated Costs

The range of estimated annualized costs among the four SO_2 recovery processes discussed, varies from about 1.9* to 2.9 mills/kwh for a 500-mw coal-fired plant. These costs include credit of 0.76 mill/kwh for the sale of by-product acid at $20 per ton. Magnesia scrubbing with acid production at a net cost of about 1.9 mills/kwh is the least expensive of the four processes, and catalytic oxidation is the most expensive. In general, acid production is about 0.3 mills/kwh less costly on a net basis than sulfur production for a 500-mw power plant.

Obviously there may be many cases where Ohio utilities will not be able to realize these prices for by-products. In fact, with regulations forcing most utilities to take similar actions, the prices for sulfur and sulfur-containing products are almost sure to decline in the future. The first utilities that install such processes may enjoy a relatively attractive market for a while, but eventually many utilities may be forced to choose the by-product with the least costly disposal (or "haul-away") penalty.

In the long run for many utilities, the production of elemental sulfur may represent the least objectionable course of action. Sulfur is relatively harmless from an environmental standpoint and its disposal by selling even at depressed prices might obviate the costs of disposal of sludges produced by other processes.

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* Based on costs given by G. G. McGlamery, et al., "Conceptual Design and Cost Study--Sulfur Oxide Removal from Power Plant Stack Gas--Magnesia Scrubbing-Regeneration: Production of Concentrated Sulfuric Acid". Table 56, p 93, TVA Bulletin Y-61. Report No. EPA-R2-72-244 to Office of Research and Monitoring, EPA, Washington, D.C., May 1973.

U.S. MARKETS FOR SULFUR-CONTAINING COMPOUNDS

There are several sulfur-containing compounds which may be produced from the sulfur oxides in utility flue gas. These include sulfur, sulfuric acid, gypsum, ammonium sulfate, sodium sulfite, and sulfur dioxide. The potential markets for each of these compounds is discussed in the following sections.

Sulfur

Although sulfur is used for a variety of applications, the manufacture of sulfuric acid is by far the largest use, amounting to nearly 90 percent of elemental sulfur consumed in the United States. Consequently, markets for sulfur and sulfuric acid are closely related. The nonacid uses for sulfur include the manufacture of chemicals and the manufacture of refined grades of sulfur used in agriculture and in the rubber industry.

Supply

During the past 5 years, the total U. S. production of sulfur in all forms has fluctuated between 9.5 and 10.2 million long tons.*,** The high of 10.2 million long tons was reached in 1972. Total sulfur production includes elemental sulfur produced at Frasch sulfur mines, elemental sulfur recovered as by-product from petroleum refining and natural gas operations, and hydrogen sulfide and liquid sulfur dioxide recovery.

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* U.S. Bureau of Mines, Mineral Industry Survey, Sulfur in 1972 (July 2, 1973).

** All quantities of elemental sulfur are given, according to custom, in "long tons" of 2240 pounds. Quantities of other materials are given in conventional "tons" of 2000 pounds, sometimes referred to as short tons.

Historically, most of the sulfur produced and consumed in the United States has been obtained from Frasch sulfur mines. In 1970 Frasch sulfur accounted for 72 percent of domestic production of sulfur in all forms (including by-product elemental sulfur, and the sulfur values from by-product smelter acid, pyrites, and other sulfur containing compounds). In 1972, the United States was an exporter of sulfur, and Frasch sulfur accounted for only 59 percent of the apparent domestic consumption.* All of the U.S. Frasch sulfur is produced in Texas and Louisiana. The market share of Frasch sulfur has been declining with corresponding gains in by-product sulfur recovered from natural gas, from refinery operations, and from smelter gases. This trend is expected to continue.

In the 10 year period between 1962 and 1972, the recovery of elemental sulfur from natural gas and refinery gas streams increased from 0.9 to 1.9 million long tons per year. Increased recovery of elemental sulfur at refineries is anticipated. This trend will be caused primarily by ever increasing imports of high-sulfur Mideastern crude oil to U. S. refineries, although the increasing demand for lower sulfur fuels caused by environmental regulations will also contribute to the growth in recovered elemental sulfur. Increases in this recovered sulfur will be concentrated in the refining centers primarily on the Gulf Coast and at new refineries on the East Coast. This would not be expected to be a major factor in Ohio or neighboring states.

Any new supplies of by-product sulfur or other sulfur compounds originating from the electric utilities would have to compete directly with recovered sulfur or by-product sulfuric acid from other industries. Market penetration by the electric utilities would be expected primarily at the expense of the Frasch producers of new sulfur.

In Ohio there is currently very little sulfur production. A zinc smelter in Columbus produces about 60,000 tons of by-product acid,

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* U.S. Bureau of Mines, Mineral Industry Survey, Sulfur in 1972 (July 2, 1973).

or the equivalent of about 17,500 long tons sulfur per year. In addition, Ohio refineries also recover some by-product sulfur. This by-product sulfur is probably less than 30,000 long tons per year.

Supply Economics

The minimum sulfur price required to keep a Frasch mine in operation is very difficult to estimate. Each mine is a unique situation. Operating costs vary considerably. Manderson* has estimated the manufacturing costs at $7 per long ton for low-cost producers, $11 for a medium-cost, and $15 for a high-cost producer. Rising fuel costs will certainly inflate these estimates. If a 15 percent pretax return on fixed investment is added, these estimates become $10, 15 and 23 per long ton. Sales, general, and administrative expenses increase these to minimum fob prices of $14, 19, and 27 per long ton.

The current posted price for crude, bright molten sulfur, ex terminal Tampa, Florida, is $28 per long ton.** Large users probably have contracts for considerably lower prices.

Ohio utilities are among the most distant potential sources of sulfur from the large Florida and Louisiana markets. Therefore, if sulfur from electric generation plants can force closing of Frasch mines, Ohio utilities would have to compete with the most efficient Frasch sulfur producers.

Assuming that Frasch mines would not be closed until revenues failed to cover cash expenses, and assuming that Manderson's estimates of manufacturing cost approximate cash expenses of producing Frasch sulfur, Ohio utilities would have to offer sulfur at $11 per long ton delivered in Louisiana. Shipping costs to Louisiana by barge on the Ohio and Mississippi Rivers are estimated to be about $6-7 per ton, and

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* Manderson, M. C., "The Sulfur Outlook", Sulfur & SO_2 Developments, American Institute of Chemical Engineers, New York, 1971. He also estimated 3.0 million long ton capacity for low cost, 5.8 million for medium, and 2.8 million for high cost.

** Chemical Marketing Reporter, 204, 35 (July 30, 1973).

using Manderson's estimate of $4 per long ton for sales and administrative expense, it appears that Ohio sulfur might be sold on the Gulf Coast if essentially no netback were required to justify the project.

Some industry observers believe that virtually all Frasch mines would close if the price of sulfur were to fall below $15 per lon ton. At this level, utilities on the Ohio River might obtain a small netback for sulfur.

Utilities not located on the Ohio River would be at a considerable disadvantage, since transportation to the river and construction of a trans-shipment terminal would be required. An alternative would be rail shipment of molten sulfur from Ohio to Florida. This would cost an estimated $13 to $15 per long ton, assuming commodity rates could be negotiated. The existing class rates, however, are $29 to $31 per long ton by rail.

Major Uses for Sulfur

Since most sulfur consumption in the United States is to make sulfuric acid, sulfur and sulfuric acid would be the two products in greatest demand which could be manufactured most logically in large volume by electric utilities.

There is already large production of sulfuric acid on the Gulf Coast, but there are numerous utilities, which also burn high sulfur coal, in states between Ohio and the Gulf Coast. Transportation costs would be lower from these utilities to the Gulf Coast markets, and therefore they would have a competitive advantage for shipments in that direction. A rough estimate of the supply and demand for sulfur in those states where the pollution control regulations are expected to require stack gas desulfurization is summarized in Table 4. This analysis indicates that if some sulfur were not recovered by those utilities nearer to the market because they choose to use some other method of emission control, there would then be a potential market for sulfur from Ohio utilities. In order to penetrate this market, Ohio utilities would have to deliver sulfur on the Gulf Coast at prices competitive with Frasch sulfur.

TABLE 4. ESTIMATED SULFUR BALANCE IN SELECTED STATES, 1971
(Sulfur or Sulfur Equivalent units, 1000 long tons; Sulfuric Acid units, 1000 short tons)

State	Sulfur Dioxide Emissions: Coal Consumed 10^6 tons	Assumed, % S	Sulfur Equivalent,	By-Product Sulfur Recovered,[b]	Sulfuric Acid Production: Total Production	Estimated Acid from Smelter Gas	Net Sulfur Consumption	Potential Sulfur Excess (Deficit)
Ohio	38.2	3	1,010		477	60	119	891
Indiana	23.0	3	630		-	-	-	630
Illinois	28.1	3	770	c	960	145	227	543
W. Virginia	16.3	3	440			-		
Kentucky	20.3	3	550		1,713[a]	-	126[a]	1,264[a]
Tennessee	14.7	3	400			1,260		
Miss. & Okla	0.5	-	-	c		-		
Missouri	11.8	2.8	300	c	502	175	91	209
Arkansas	-	-	-	c	305	-	85	(85)
Alabama	16.1	2.5	360		376	-	104	256
Louisiana	-	-	-	c	3,553	-	986	(986)
Texas	-	-	-	770.4	2,204	-	615	155
Florida	5.1	3	140	3.8	8,194	-	2,278	(2,134)
Grouped States[c]				378.0[c]				378.0[c]
Total for States Closer to Fla. Than Ohio			3,590	1152.2			4,512	230

(a) Composite sulfuric acid production of W. Va., Ky., Tenn., Miss., and Okla.
(b) By-product sulfur equivalent from all sources directly competitive with potential recovery from SO_2 emissions.
(c) Combined by-product sulfur from States of Ill., Miss., Okla., Mo., Ark., and La.

Non-Acid Uses for Sulfur

The non-acid uses for sulfur account for about 10 to 13 percent of total consumption. The major industries using elemental sulfur for non-acid purposes include the pulp and paper industry, carbon disulfide, rubber, sugar, starch, malt, dye stuffs, and agricultural chemicals. Of these uses, only the manufacture of carbon disulfide and use of sulfur in the rubber industry appear to be of significant size as possible outlets for sulfur manufactured in Ohio.

Carbon Disulfide. Carbon disulfide accounts for approximately 3 percent of the sulfur consumption in the United States. Traditionally, carbon disulfide was manufactured by the reaction of sulfur and charcoal. With the possible exception of a small plant operated by Pennwalt in Houston, Texas, all U.S. manufacturers use a newer process in which methane and sulfur are catalytically reacted in the vapor phase. This process produces carbon disulfide and hydrogen sulfide. The hydrogen sulfide then is converted to sulfur for recycling.

Efforts to reduce sulfur emissions from carbon disulfide and sulfur plants should result in recovery and utilization of virtually all sulfur employed in the reaction. Therefore, one would expect sulfur consumption to be very near the stoichiometric requirements of 0.842 pound sulfur per pound carbon disulfide. For the purposes of calculation, sulfur consumption has been assumed to be 0.85 pound per pound carbon disulfide. Historically, it is believed that this value has been closer to 0.9 pound per pound, but this was before the strict enforcement of pollution control regulations.

There are two major uses for carbon disulfide. The manufacture of rayon and cellophane accounts for about 65 percent of all carbon disulfide consumption. Manufacture of carbon tetrachloride accounts for about 25 percent, and miscellaneous uses such as manufacture of rubber chemicals accounts for the remaining 10 percent*. In the manufacture of carbon tetrachloride from carbon disulfide, sulfur is regenerated and net consumption is low.

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* Oil Paint, & Drug Reporter, 202, 9 (July 24, 1972).

There are 5 plants in the United States manufacturing carbon disulfide. The total capacity of these plants is 850 million pounds per year. Two of these plants, with a capacity of 240 million pounds, are located in West Virginia near the Ohio River. In 1972, the demand for carbon disulfide was estimated at 775 million pounds,* or about 91 percent of total capacity. Assuming that the West Virginia plants operated at the national average fraction of capacity, and assuming they consumed 0.85 pound sulfur per pound carbon disulfide, then in 1972 they would have consumed 186 million pounds or 83,000 long tons sulfur. Actual demand for sulfur at these plants was probably much lower, since one is associated with a carbon tetrachloride plant. The growth rate for carbon disulfide is expected to be about 2 percent per year over the next 5 years.

Rubber Processing. Although rubber processing accounts for a small fraction of the total sulfur consumption in the United States, a large fraction of the rubber products manufactured in the United States are made in and near Ohio. In 1967 for example 26.7 percent of the value of rubber goods shipped in the United States were manufactured in Ohio, and 41 percent of the national total were made in the East North Central census region.**

The quantities of sulfur required in any particular rubber recipe will vary depending upon the type of rubber to be vulcanized and the desired properties of the finished product. In general, the soft rubber products contain less than 3 parts sulfur per hundred parts rubber, while hard rubber products may obtain up to 60 parts per hundred. Less sulfur is consumed in vulcanizing synthetic rubbers than in vulcanizing natural rubbers to obtain the same properties. Thus as natural rubber diminishes in importance compared with synthetic rubber, the overall

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* Oil Paint, & Drug Reporter, 202, 9)July 24, 1972).

** U.S. Department of Commerce, 1967 Census of Manufacturers, p 30A-9.

consumption of sulfur per pound of rubber will decrease. Furthermore, the use of other chemicals as accelerators in the vulcanizing process decreases the amount of sulfur required.

There is a variety of opinion on the average amount of sulfur consumed per pound of rubber. The opinions vary from 3 to 4 parts per hundred for natural rubber and 1.5 to 3 parts per hundred for synthetics. For the purposes of estimating, about 3 parts per hundred was assumed to be the average for all rubber. Based on this assumption, and on estimated 1973 consumption of rubber*, the current estimated consumption of sulfur for rubber vulcanizing in Ohio is about 24,400 long tons of sulfur per year.

Although elemental sulfur can be used without special processing for most applications, special grades of sulfur are required for use in rubber vulcanization. These special grades may be ground or triturated to reduce particle size or some times sublimed and extracted with carbon disulfide to make insoluble sulfur.**

The special grades of sulfur used by the rubber industry are sold by a number of chemical companies. The major suppliers of rubber grade sulfur are C. P. Hall, Harwich Chemical, Monsanto, FMC (Niagara Chemical Division), H. M. Royal, Smith Chemical, and Stauffer.

Minor Uses. The pulp and paper industry consumes some elemental sulfur for the preparation of sulfide chemicals used in the pulping operation. This application is discussed in the following section on sodium sulfite.

Elemental sulfur is used in the manufacture of a variety of dyes and chemicals. These markets are small and diverse when compared with other market segments discussed in this report.

Sulfur is used to generate sulfur dioxide which finds application in bleaching malt and beet sugar juice, and in the production of cornstarch.

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* Rubber Age, p 29 (January 1973).

** For more details see Varnat, P. "Refined Sulfur and Special Grades", Sulfur, p 65 (May/June 1967).

The traditional agricultural use for sulfur has been in the manufacture of fungicides and insecticides. These applications require specially processed sulfur and have been declining in their significance. Although the use in the manufacture of insecticides has been declining, there may be a slight increase in agricultural use of sulfur for the manufacture of sulfur-coated urea. A process for the manufacture of sulfur-coated urea for use as fertilizer has been developed by the Tennessee Valley Authority and there has been some commercial interest in this fertilizer. It is anticipated, however, that this sulfur will be consumed on the Gulf Coast near urea manufacturing facilities. Furthermore, it is anticipated that it will remain a specialty fertilizer for use on turf and pastures rather than gain widespread application.

Summary of Sulfur Markets

Nearby markets for elemental sulfur in Ohio are limited. It appears that there is now a market for about 110,000 long tons in Ohio at sulfuric acid plants. In addition, the DuPont plant in Wurtland, Kentucky (about 15 miles upstream from Portsmouth, Ohio) consumes an estimated 30,000 long tons. If rubber grade sulfur for use in Ohio were manufactured from Ohio by-product sulfur, this would add about 24,000 long tons, and Ohio utilities might supply up to 40,000 long tons for nonacid chemical uses. Thus the maximum nearby market for by-product sulfur from Ohio would be about 200,000 long tons per year in 1975.

It will be difficult to penetrate rubber and chemical markets for sulfur. Furthermore, the installation of a new smelter near Louisville, Kentucky will reduce the consumption of elemental sulfur for sulfuric acid manufacture in the Ohio River valley. Therefore, a more realistic estimate of nearby available markets for elemental sulfur produced at Ohio utilities would be 120,000 long tons per year. This would be diminished by any by-product sulfuric acid from Ohio utilities. If sulfur from Ohio utilities can be delivered in Florida and Louisiana at costs competitive with Frasch producers, these markets can absorb essentially all sulfur removed from Ohio utility flue gas.

Sulfuric Acid

Supply and Demand in the North Central States

Although there has been little growth in the production of new sulfuric acid* in the period from 1966 to 1971, there has been a shift in the geographical location of the acid production away from the northern states towards the Gulf Coast. During the period from 1966 through 1971 the production of new acid in the North Central states declined from 4.5 million tons to 3.4 million tons. During the same period, production of the new acid in Florida and Louisiana increased from 8.8 million tons to 11.7 million tons.

In 1971, Florida consumed an estimated 2,278,000 long tons of elemental sulfur for acid manufacture and Louisiana consumed 986,000 long tons. Additional acid capacity is under construction in these states.

This shift in the location of the sulfuric acid production is, for the most part, caused by changes in the phosphate fertilizer industry, as discussed later.

Supply and Demand in Ohio

Because of the relatively high transportation costs for overland shipments of sulfuric acid, new sulfuric acid generally is consumed near the production site. By-product sulfuric acid can be shipped over longer distances and may be consumed several hundred miles from its point of origin. By-product sulfuric acid from electric utilities in Ohio would not be expected to displace by-product sulfuric acid generated from other sources. Therefore, for practical purposes, the available market for by-product sulfuric acid from utilities would be limited to the

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* New acid includes all acid manufactured directly in sulfuric acid plants, including acid from smelter gas and acid sludge. Some spent sulfuric acid recovered from chemical processes (e.g., drying nitric acid) is sold for certain applications. This used acid is excluded from new acid statistics.

markets normally served by sulfuric acid manufactured in or near Ohio from elemental sulfur. It is reasonable to use the production of sulfuric acid from elemental sulfur as a good estimate of the Ohio demand for acid.

The reported production of sulfuric acid in Ohio has varied from a high of 704,000 tons in 1965 to a reported low of 477,000 tons in 1971 (See Table 5). It is believed that the 1971 figure may have omitted production from one sulfuric acid plant. In 1972, Ohio production of sulfuric acid was 560,000 tons.* Of this, American Smelting and Refining Company makes about 60,000 tons acid per year from smelter gas. In addition, an estimated 115,000 tons is made by burning sludge which is recycled from petroleum refineries. This leaves about 385,000 tons sulfuric acid produced from elemental sulfur in Ohio. The Ohio production of sulfuric acid would consume approximately 112,000 long tons sulfur. As estimated 1,090,000 long tons of sulfur were emitted to the atmosphere in 1971 by Ohio utilities.

Central Ohio. The only acid capacity in Central Ohio is that based on smelter gas. This smelter, located in Columbus, has an annual capacity of 64,000 tons acid. It serves central Ohio markets as well as shipping to more distant points within the state. As would be expected, the remaining sulfuric acid plants in Ohio are located in the industrialized areas which are generally near the borders (See Table 6).

Northern Ohio. The installed sulfuric acid capacity in northern Ohio is slightly over 600,000 tons per year, including the estimated 115,000 tons per year manufactured from acid sludge. It appears that the sulfuric acid plants in Ohio which burn elemental sulfur have been operating at near 50 percent capacity. Therefore, it is estimated that approximately 240,000 tons sulfuric acid are manufactured in northern Ohio from elemental sulfur. Some of this elemental sulfur may be by-products from Ohio refineries. The actual market for sulfuric acid in northern Ohio may be somewhat larger, since by-product sulfuric acid from Canadian smelters has reportedly been imported into Cleveland. These Canadian imports are believed to be small, however.

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* U.S. Bureau of Census, unpublished data.

TABLE 5. PRODUCTION OF SULFURIC ACID IN OHIO

1,000 tons new 100% H_2SO_4

Year	New Production	Shipments[a]	Number of Establishments
1962	661.5	512.1	
1963	659.1	486.4	14
1964	674.8	521.8	12
1965	704.0	535.1	12
1966	689.0	554.7	11
1967	652.6	520.3	11
1968	628.4	519.9	10
1969	579.7	500.4	9
1970	641.6	431.7	8
1971	477.0[b]	378.4[b]	7[b]
1972	560.3		

Source: U.S. Department of Commerce, Current Industrial Reports M28A, Sulfuric Acid.
(1972 from unpublished Bureau of Census data)

(a) Includes interplant transfers.

(b) May not include production from Coulton Chemical Company.

TABLE 6. OHIO SULFURIC ACID PLANTS

Company/Location	Capacity (1000 tons/yr, 100% basis)	Raw Materials
Allied Chemical Corp.		
Cleveland	130	elemental sulfur
American Cyanamid		
Hamilton	90	"
American Smelting & Refining Co.		
Columbus	64	smelter gas
Coulton Chemical Co.		
Toledo	174	acid sludge, H_2S and elemental
Agrico Chemical Co. (Subsidiary Williams Co.)		
Cairo (near Lima)	43.5	elemental sulfur
DuPont		
Cleveland	215	"
North Bend (near Cincinnati)	175	"
Minnesota Mining & Manufacturing Co.		
Copley	60	"
Total	951.5	

Not all sulfur-burning capacity can be eliminated. Because there is no flexibility in production of by-product sulfuric acid, sulfuric acid manufactured from sulfur must be available to compensate for fluctuations in supply and demand. Therefore, it appears that approximately 200,000 tons by-product sulfuric acid could be sold from a northern Ohio utility site each year.

Southern Ohio. The only two sulfuric acid plants located in Southern Ohio are the American Cyanamid Plant in Hamilton and the DuPont plant near Cincinnati. There are, however, several sulfuric acid plants in neighboring states located in the Ohio Valley which would compete in the same markets as a sulfuric acid plant in southern Ohio. (See Table 7.)

Due to the lower costs of barge shipments compared with overland shipments, it is feasible to ship sulfuric acid along the river to fairly distant large customers. To serve smaller customers or customers inland from the river, a transhipment terminal is required and the distribution costs are increased considerably. Because of the relatively low cost of barge transportation compared with overland transportation, these sulfuric acid plants along the river are in competition. In order to compete effectively in southern Ohio and in the Ohio River Valley, a sulfuric acid plant manufacturing sulfuric acid by-product from utility operations would have to be located on the Ohio River.

The installed sulfuric acid capacity on the Ohio River and its tributaries between Newell, Pennsylvania and Calvert City, Kentucky is 1,165,000 tons per year. The sulfuric acid production and consumption in the Ohio River Valley and its tributaries is estimated to be about 700,000 tons per year.

Upstream from Ohio, St. Joe Minerals produces about 300,000 tons sulfuric acid annually from smelter gas at Monaca, Pennsylvania. This will be increased to 350,000 tons in the late 1970's. In addition, U.S.S. Chemicals may be manufacturing up to 50,000 tons sulfuric acid from hydrogen sulfide and sulfur recovered from coke oven gases at Pittsburgh.

TABLE 7. SULFURIC ACID PLANTS IN NEIGHBORING STATES

Company/Location	Annual Capacity, 1,000 tons		Raw Materials
	On Ohio River and Tributaries	Other	
Allied Chemical Corp.			
Buffalo, N.Y.	-	195	sulfur, sludge, H_2S
Detroit, Mich.	-	200	sulfur, sludge
Newell, Pa.	250	-	sludge, pyrites
Nitro, W. Va.	140	-	sulfur
Detroit Chemical Works			
Detroit, Mich.	-	35	sulfur
DuPont			
Wurtland, Ky.	200	-	sulfur, sludge
International Minerals & Chemicals			
Indianapolis, Ind.	-	65	sulfur
Pennwalt Corp.			
Calvert City, Ky.	50	-	sulfur
St. Joe Minerals Corp.			
Monaca, Pa.	300	-	smelter gas
U.S.S. Chemicals			
Pittsburgh, Pa.	50	-	sulfur, hydrogen sulfide
Williams Co.-Agrico Division			
Bay City, Michigan	-	40	sulfur
Witco Chemical Corp.			
Petrolia, Pa.	-	45	sludge

Downstream from Ohio, American Smelting and Refining Company is planning to build a zinc smelter in Breckinridge County, Kentucky. This site is on the river between Louisville and Owensboro. This project is still in the planning stages, but the plant is expected to be onstream in mid or late 1976. About 360,000 tons by-product acid will be produced at this smelter. Some of the acid from this new smelter will no doubt be sold inland and some will be moved down river, possibly to be sold along the Mississippi as well as along the Ohio. It must be anticipated, however, that some of the by-product acid from the new smelter will be sold up river.

Finally, some sulfuric acid capacity from elemental sulfur will be required to meet fluctuations between the supply of by-product acid and the demand. A temporary oversupply of by-product acid could cause monumental storage logistics and disposal problems.

When all these factors are considered, it appears that there may be a market for between 100,000 and 150,000 tons by-product sulfuric acid from utilities located along the Ohio River.

Demand According to End Use

Sulfuric acid is one of the most versatile chemicals manufactured in the United States. Traditionally it has been the least expensive acid available. Further reduction in the price of sulfuric acid would not, therefore, be expected to increase the potential market. There is one exception to this price inelasticity, however, and that is in the use of sulfuric acid for a leaching low-grade copper oxide ores. The availability of by-product sulfuric acid from Western copper smelting operations has made the recovery of copper from low-grade copper oxide ores feasible.

The major end uses for sulfuric acid are summarized in Table 8, which shows that, over half the sulfuric acid used in the United States is consumed in the manufacture of phosphate fertilizers. The remaining sulfuric acid is used for a wide variety of applications. Some of the more important applications are discussed below.

Fertilizer. The trend in the phosphate fertilizer industry has been to build large efficient plants to manufacture phosphate fertilizers on the Gulf Coast. Most of these plants are located in Florida and

TABLE 8. SULFURIC ACID END-USE PATTERN, 1970

	Thousand tons (100% basis)
Fertilizer	
Phosphoric acid products	13,750
Normal superphosphate	1,240
Cellulosics	
Rayon	520
Cellophane	170
Pulp and paper	600
Petroleum alkylation	2,400
Iron and steel pickling	800
Nonferrous metallurgy	
Uranium ore processing	300
Copper leaching	350
Chemicals	
Ammonium sulfate–coke oven	500
synthetic	480
chemical byproduct	190
Chlorine drying	150
Alum	600
Caprolactam	260
Dyes and intermediates	370
Detergents, synthetic	400
Chrome chemicals	100
HCl	150
HF	880
TiO_2	1,440
Alcohols	1,800
Other chemicals	380
Industrial water treatment	200
Storage batteries	140
Other processing	470
Total	28,640

Source: McGlamery, G.G., et al, "Sulfur Oxide Removal from Power Plant Stack Gas - Magnesia Scrubbing", TVA Bulletin Y-61, p 101 (May, 1973).

Louisiana. Consequently, these two states are the two largest producers of sulfuric acid. These Gulf Coast fertilizer plants manufacture concentrated fertilizers like triple superphosphate and diammonium phosphate, both of which require manufacture of intermediate phosphoric acid. Not only are economies of scale realized by the construction of large plants, but shipping costs are minimized because the concentrated fertilizers produced in these plants contain more phosphate than does the phosphate rock from which they are manufactured.

In contrast, there is some manufacture of normal superphosphate in Ohio. Normal superphosphate is a low analysis fertilizer containing less phosphorus per ton than the phosphate rock. Therefore, normal superphosphate is generally manufactured near the farmer. The trend has been to retire these northern superphosphate plants and to replace them with the large concentrated phosphate fertilizer plants on the Gulf Coast.

There are mixed opinions whether this trend to close the normal superphosphate fertilizer plants in the North and expand production on the Gulf Coast will continue. Some industry observers expect the trend to continue until the northern fertilizer plants are all abandoned. This conclusion would certainly result if northern states were to require these fertilizer manufacturers to install equipment to control fluoride emissions to the air. Such emissions can be economically controlled only in large modern plants. Even without the imposition of fluoride emission controls on these modern plants, the economics of the fertilizer industry would indicate that at current transportation and sulfuric acid prices, the normal superphosphate plants will be gradually retired. It is now more economic to make a concentrated fertilizer near the source of phosphate rock and ship it to the farm areas than to ship the rock and make a less concentrated fertilizer near the farmer. Finally, farmers and bulk fertilizer blenders have become accustomed to the convenience and economies obtained by use of higher analysis fertilizers. It would be difficult to reverse the trend toward use of higher analysis fertilizers.

The opposing view states that the closure of normal superphosphate plants has ceased, that the inefficient plants have been already shutdown, and that the northern fertilizer industry may even grow as a result of low cost sulfuric acid obtained as by-product from electric utilities. It does

appear that if an Ohio fertilizer manufacturer could obtain sulfuric acid at essentially no cost, then normal superphosphate could be manufactured for a lower cost per unit of phosphorus than a more concentrated fertilizer could be delivered from the Gulf Coast. When the cost of distributing fertilizer to the retailer and delivering to the farmer are considered, however, the costs per unit of nutrient are very close.

As sulfur dioxide is removed from utility flue gas, the soils in the North Central states may become sulfur deficient. There is already a small region of sulfur-deficient soils in southwestern Indiana, and there are very limited areas of coarse textured soils, which are the most likely to become sulfur deficient, near the northern edge of Ohio.* Normal superphosphate does have the advantage of containing sulfur as well as phosphorus, whereas the more concentrated phosphate fertilizers do not. Of course, there are other chemicals like ammonium sulfate, sulfur, and gypsum which can be used to supply necessary sulfur to the soil.

Although a detailed analysis of each specific situation is required to determine the fate of a particular venture, it seems probable that the economic advantage in a free market of normal superphospnate compared with higher analysis fertilizers will be at best marginal, and that easier handling of the higher analysis materials will perpetuate the decline in the manufacture of normal superphosphate in the northern states.

One possibility for a power plant located along the Ohio River would be the manufacture of sulfuric acid, to be used on-site for the manufacture of phosphoric acid and concentrated phosphate fertilizers. A very preliminary analysis indicates that phosphoric acid and diammonium phosphate fertilizer could be manufactured on the Ohio River for about the same price as it can be manufactured and shipped from the Gulf Coast, assuming that the sulfuric acid would be available at no cost in Ohio and the sulfur would cost about $18 per long ton on the Gulf Coast. The minimum economic size of a phosphoric acid plant would probably have a capacity of about 700 tons P_2O_5 per day, or 230,000 tons per year. By coincidence, this happens to be the 1972 consumption of phosphate fertilizers in Ohio.** This capacity would correspond to about 438,000 tons sulfur dioxide removed from utility flue gas.

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* Beaton, J.D., S.L. Tisdale, and J. Platou, "Crop Responses to Sulfur in North America", Technical Bulletin 18, The Sulfur Institute, Washington, D.C.

** Hargett, N.L., 1972 Fertilizer Summary Data, National Fertilizer Development Center, Tennessee Valley Authority, Muscle Shoals, Alabama.

A utility would have to work closely with a fertilizer manufacturer in developing a venture to manufacture concentrated phosphate fertilizers in Ohio. Furthermore, the utility and the fertilizer operation would probably have to be located on the Ohio River in order to obtain the low transportation rates needed to make such a project viable.

Although no single Ohio utility plant located on the Ohio River emits over 400 tons per day of sulfur dioxide, there are locations where two large power plants, which together emit about the quantity of sulfur dioxide needed for such a venture, are located in close proximity. The Cincinnati and Steubenville areas appear to be likely locations for such a venture.

These areas are not mentioned to demonstrate that such a venture would, in fact, be practical. An intensive and detailed study would be required before such a conclusion could be drawn. However, such a venture would probably not be practical for any other groups of Ohio utilities. In evaluating such a venture, the potential water pollution problems associated with fertilizer manufacture would also have to be considered. The manufacture of phosphoric acid generates large quantities of gypsum, and a very large gypsum pond area containing acidic water would be required.

Petroleum Refining. Petroleum alkylation ranks second to fertilizers as the largest consumer of sulfuric acid, yet petroleum alkylation accounts for only about 8 percent of consumption. Sulfuric acid is used by Standard Oil and Sun Oil Company in their Toledo refineries for alkylation. An estimated 100,000 tons sulfuric acid are consumed each year in Ohio in petroleum operations. Nevertheless, the sulfur values from the sulfuric acid used in petroleum refining are recovered in the form of acid sludge which is returned to sulfuric acid plants to be burned and reprocessed into new sulfuric acid. Therefore, this portion of the apparent end-use market is not available for penetration by sulfuric acid from utilities or other sources.

In addition to the acid sludge from Ohio refineries, an estimated 15,000 tons acid per year are believed to be reprocessed in an Ohio sulfuric acid plant for a Michigan refinery. Thus an estimated 115,000 tons per year sulfuric acid are made in Ohio from acid sludge.

Titanium Dioxide. The third largest consumer of sulfuric acid is the manufacture of titanium dioxide by the sulfate process which uses 4 to 4.5 tons of 100 percent sulfuric acid per ton of titanium dioxide. Although there are two titanium dioxide plants in Ashtabula, Ohio, both use the competing chloride process. The chloride process does not require sulfuric acid. All of the plants using the sulfate process are located on the East Coast except a plant of NL Industries in St. Louis, Missouri, with a rated capacity of 108,000 tons TiO_2 per year. Its acid is supplied from a captive acid plant burning sulfur to SO_2, with an annual capacity of 350,000 tons.* None of these plants is considered close enough to Ohio utilities to provide markets for by-product sulfuric acid generated in Ohio.

Steel Pickling. During the hot rolling of steel, an oxide scale forms on the surface. Before further finishing, such as cold rolling, this scale must be removed. Prior to 1966, sulfuric acid was the principle means for descaling of hot rolled steel. Since then the hydrochloric acid descaling process has displaced much of the sulfuric acid formerly used in descaling steel. Hydrochloric acid offers a number of advantages over sulfuric acid for continuous pickling of steel. These include:

(1) Better quality steel

(2) Lower cost operation

(3) Ability to regenerate acid.

The cost savings from use of hydrochloric rather than sulfuric acid result from increased speed of the pickling operation. Line speed increases of 25 to 50 percent are claimed for most pickling lines using hydrochloric rather than sulfuric acid.

Disposal of waste pickle liquor presents a potential water pollution problem. Technology is available to regenerate hydrochloric acid from spent pickle liquor.** Recovery of sulfuric acid from spent

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* Stanford Research Institute, Directory of Chemical Producers, 1973, p 857

** For instance, the Woodall-Duckham Process, licensed by Pennsylvania Engineering Corporation, Pittsburgh, Pennsylvania.

pickle liquor is considerably more difficult, and according to the best information available, has not been adequately proven in commercial practice in the United States.

Although the use of sulfuric acid for steel pickling has declined in recent years, industry observers believe it has now stabilized. Pickling is an important use of sulfuric acid in Ohio and the neighboring area. No regional data were easily available, but it is estimated that somewhat less than 100,000 tons were used in this area of the 800,000 tons listed as the U.S. pickling acid consumption in Table 8.

Hydrofluoric Acid. In the United States an estimated 920,000 tons sulfuric acid was consumed in 1973 for the manufacture of hydrofluoric acid. Demand has been projected to grow at an annual rate of 6.5 percent per year through 1977.* There is only one hydrofluoric acid plant in Ohio. It is owned by Harshaw Chemical Company in Cleveland and has an annual capacity of 18,000 tons (which would consume about 44,000 tons sulfuric acid). The industry has been running near capacity. In addition, there is a plant with an annual capacity of 20,000 tons in Nitro, West Virginia and another in Calvert City, Kentucky with a capacity of 25,000 tons. Both of these are located adjacent to captive sulfuric acid plants. It would probably be very difficult to sell by-product acid from Ohio utilities at these locations, although there might be an opportunity to dispose of surplus acid for little more than shipping and administrative costs.

Feasible Market Area for Ohio Utilities

Gulf Coast Markets. There are several factors which will tend to limit the ability of Ohio utilities to penetrate distant sulfuric acid markets, especially the large markets on the Gulf Coast. The first and most obvious limitation to penetration of Gulf Coast markets would be in

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* Chemical Marketing Reporter, 203, 9 (February 5, 1973).

the transportation cost. Sulfuric acid weights about 3 times as much as the sulfur contained in the product. Therefore, acid transportation costs will be much higher than sulfur transportation costs. Barge transportation of acid to the Gulf Coast is estimated to be about $6 to $7 per ton.

As the cost of sulfur on the Gulf Coast is reduced, the manufacturing cost for sulfuric acid approaches the shipping cost from Ohio. At $15 per long ton for sulfur, the manufacturing cost for sulfuric acid in a modern efficient plant would be about $6.40 per ton (excluding return on capital). Even with sulfur at $25 per long ton, sulfuric acid could be manufactured at a cost of about $9.30 per ton.

A second factor which will limit the long-distance shipments of sulfuric acid manufactured at utilities would be the required storage capacity. Sulfuric acid is more expensive to store than sulfur. Electric utilities operate more or less continuously, and acid would be produced throughout the year. Seasonal variations in the demand for electricity would result in corresponding variations in the production of acid. Such variations would probably not correspond to the customer's demand for acid. Storage capacity would be required to take care of these imbalances. Furthermore, additional storage capacity would be required as a contingency for unexpected interruptions in the transportation system.

A third factor which will limit the ability of Ohio utilities to ship sulfuric acid or magnesium sulfite to Gulf Coast markets relates to the energy crisis. The Gulf Coast manufacturers of sulfuric acid have integrated the sulfuric acid manufacture with fertilizer-manufacturing operations. The heat released by burning sulfur to make sulfuric acid is converted to steam which is then used in the fertilizer manufacture. For every ton of sulfuric acid manufactured, about 1.1 tons steam is produced.* To replace this steam, fuel containing about 2.64 million Btu per ton acid would be required. Because of the gas shortage, a Gulf Coast fertilizer manufacturer would probably have to rely upon No. 2 fuel oil to replace this process steam. This fuel oil currently sells for about $0.15 per gallon or $1.08 per

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* Bixby, D.W., D.L. Rucker, and S.L. Tisdale, Phosphatic Fertilizers, The Sulphur Institute, Technical Bulletin 8, Washington, D.C. (1966).

million Btu. Thus the increased fuel cost from purchasing acid rather than manufacturing it on site would be $2.85 per ton acid. In addition, significant plant modifications would probably be required in order to burn fuel oil rather than obtain this heat from burning sulfur. Therefore, the by-product sulfuric acid from utilities would probably have a penalty of at least $3.00 per ton. However, the difficulty in obtaining fuel on the Gulf Coast, as well as other parts of the country, might override current economic considerations. All factors considered, it appears that at present it is not economically attractive to ship sulfuric acid from Ohio to the Gulf Coast.

Nearby markets. If it is economically feasible for Ohio utilities to recover sulfur from flue gas in the form of sulfuric acid, then it will also be feasible for utilities in neighboring states where high-sulfur coal is also burned to generate electricity. Since more sulfur is emitted to the atmosphere in Ohio and neighboring states than is consumed in these states in the form of sulfuric acid, the markets available to Ohio utilities for marketing sulfuric acid in nearby states may be limited. If it were not for this potential competition from other manufacturers of by-product sulfuric acid, it would probably be feasible to ship by-product acid over longer distances to penetrate markets in neighboring states. The actions of the utilities in surrounding states, as well as the variations in the regulations in such states, will determine to what degree the market outside of the State of Ohio can be penetrated.

Transportation costs for distances up to 200 miles are fairly low (See Figure 5) and should not limit nearby marketing efforts. Some smelters such as Copper Hill in Tennessee currently ship and market a portion of their by-product acid production 400 miles or more in jumbo tank cars, but they have not yet encountered competition from other by-product acid producers nearer to the market.

Summary of Sulfuric Acid Markets

There may be an opportunity for by-product sulfuric acid to displace some of the estimated 240,000 tons sulfuric acid now manufactured in northern Ohio. Some production from elemental sulfur will have to be retained to provide flexibility in the operations. Thus, the

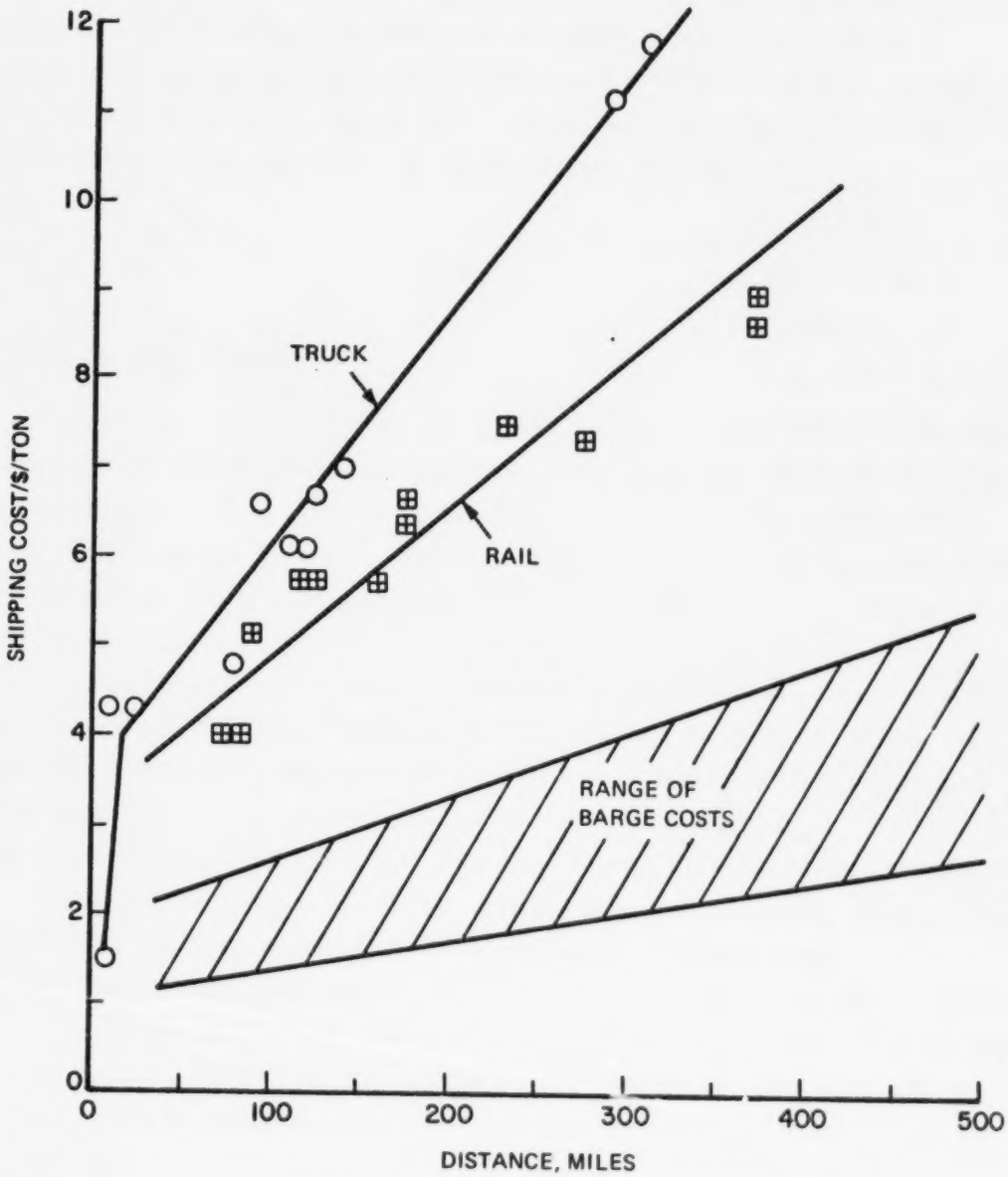

FIGURE 5 . SULFURIC ACID SHIPPING COST

estimated potential market for by-product sulfuric acid from utilities in northern Ohio is about 150,000 tons per year. In southern Ohio, a utility located on the Ohio River could probably sell between 100,000 and 150,000 tons per year. It is not believed economically attractive to ship sulfuric acid to the Gulf Coast markets from Ohio.

Gypsum

Applications and Demand

By far the largest use of gypsum in the United States is in the manufacture of gypsum board and plaster. For these applications, the gypsum is calcined and a fine product is preferred. A typical calcined product for wallboard manufacture would have at least 85 percent smaller than 100 mesh. These calcined products represent over 70 percent of the total gypsum consumption.

The second major use for gypsum is as a portland cement retarder. This application typically consumes between 18 and 22 percent of the total gypsum used in the United States. The materials handling equipment used by the cement industry is designed to handle crushed gypsum in the size range between one quarter and 2 inches, with an average size between one-half and three quarter inch. In order to be used as a cement retarder, by-product gypsum would have to be pelletized to achieve the proper size.

The third major application for gypsum is agricultural. Gypsum is used as a source of sulfur in sulfur deficient soils. Agricultural gypsum accounts for 7 to 8 percent of the national consumption, but most of this consumption is in California and, to a lesser extent, in the Southeastern United States.

As can be seen in Table 9, agricultural gypsum sales in the East North Central Region of the United States (as reported by the Bureau of Mines) are very small. U.S. Department of Agriculture reports even lower

TABLE 9. 1972 SALES OF GYPSUM AND GYPSUM PRODUCTS--
EAST NORTH CENTRAL CENSUS REGION

	Tons
Uncalcined	
Portland cement retarder	557,845
Agricultural	10,717
Other	24,280
Total Uncalcined	592,842
Calcined	
Building plasters	163,345
Industrial plasters	87,262
Board products	2,195,527
Total Calcined	2,446,134
Total Gypsum and Gypsum Products	3,038,976

Source: U.S. Bureau of Mines, Gypsum in the Fourth Quarter 1972, Mineral Industry Survey (March 5, 1973).

agricultural consumption of gypsum for the region. Consumption of agricultural gypsum in Ohio has declined from 78 tons in fiscal 1969 to zero in fiscal 1972.* Unless soils in Ohio become sulfur deficient, agricultural use of gypsum in Ohio will remain insignificant.

In the East North Central region, about 80 percent of the gypsum consumed is calcined to make gypsum board and plaster products. Miscellaneous uses of gypsum account for only 1 percent of the total consumption.

Market Growth

Historically, there has been little growth in gypsum products during the past decade (see Table 10). Total U.S. consumption has generally remained between 15 and 17 million tons per year. In 1972, however, consumption spurted to 20 million tons. This increase in consumption accompanied a significant increase in construction activity. Many economists are expecting a decline in housing starts in 1973 and 1974. The long term growth in housing starts between 1972 and 1980 has been projected to be about 1 percent per year.**

It is of interest to note that much of the increased production of crude gypsum in 1972 came from domestic mines. This indicates considerable flexibility and unused capacity. In addition, the wallboard plants were able to increase production significantly without any increase in capacity. There have been no new wallboard plants constructed during recent years, although at some locations the equipment speed has been increased. At many wallboard plants, extensive overtime was used during 1972 to meet the increase in demand.

Ohio Markets

There are two gypsum mines located in Ohio. Both of these are in Ottawa County. One is a pit mine operated by Cellotex, while the other is an underground mine operated by U.S. Gypsum. Production figures on

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* U.S. Department of Agriculture, "Commercial Fertilizers Consumption in the United States", for fiscal years 1970, 1971, 1972, Table 5.

** U.S. Department of Commerce, "U.S. Industrial Outlook 1973", p 3, U.S. Government Printing Office, Washington, D.C.

TABLE 10. U.S. AND OHIO GYPSUM STATISTICS (Thousands Short Tons)

	1957-61 av.	1962	1963	1964	1965	1966	1967	1968	1969	1970	1971	1972
Crude gypsum mined	9,804	9,969	10,388	10,684	10,033	9,647	9,393	10,018	9,905	9,436	10,418	12,367
Crude gypsum imported for consumption	4,956	5,421	5,490	6,258	5,911	5,479	4,569	5,474	5,858	6,128	6,094	7,718
Total crude gypsum, mined & imported	--	15,390	15,878	16,942	15,944	15,126	13,962	15,492	15,763	15,564	16,512	20,085
Gypsum calcined	8,406	8,819	9,181	9,440	9,320	8,434	7,879	8,844	9,324	8,449	9,526	11,984
Gypsum calcined in Ohio	--	--	--	--	--	--	334	359	356	321	358	--

Sources: Bureau of Mines, Minerals Yearbook, Gypsum

Bureau of Mines, Minerals Industry Survey, Gypsum in the Fourth Quarter 1972 (March 5, 1973).

these mines are not available. Both companies operate nearby calcining plants, however, and it is believed that production at the mines approximates the calcining requirements.

There are three calcining plants currently operating in Ohio. These are the U.S. Gypsum plant at Gypsum, the Cellotex plant at Port Clinton, and the National Gypsum plant at Lorain. It is believed that the gypsum calcined at the first two locations is from local captive mines. The National Gypsum plant is probably supplied from mines in Michigan. More gypsum is mined in Michigan than in any other state. In 1971 the total production of calcined gypsum in Ohio was 358,000 tons, up from 321,000 tons in 1970 but about the same as the 356,000 tons calcined in 1969. A typical gypsum wallboard plant consumes 200,000 to 300,000 tons gypsum per year. This would indicate that the Ohio plants are smaller than the industry average. Any increase in capacity in the State of Ohio would probably be expansions at existing plants.

Marketing Considerations

There is virtually no merchant market in gypsum. Gypsum is mined, calcined, and sold by integrated companies. Even imported gypsum is usually from captive mines. In order to interest the major gypsum companies in by-product gypsum, it would probably have to be priced at $2.00 to $2.50 per ton in those parts of the country, like Iowa and Texas, where there are large seams of high-quality gypsum. The gypsum mined in Ohio is of lower quality, and some beneficiation is needed before processing. In Ohio, it might be possible to obtain as much as $3.00 per ton, delivered to the calcining plant. It would be unrealistic for utilities to expect to obtain the current gypsum price. The 1971 national average price for crude gypsum was $3.72 per ton.*

* U.S. Bureau of Mines, Minerals Yearbook, 1971 Preprint, Gypsum chapter.

Before by-product gypsum from flue-gas desulfurization units could be sold to a manufacturer of gypsum products, it would be necessary to determine whether such gypsum were in fact suitable for manufacture of wallboard. Although by-product gypsum is being used to manufacture wallboard in Japan, Japanese conditions are somewhat different. U.S. wallboard manufacturers suspect Japanese specifications for wallboard are less demanding than those in the United States.

National Gypsum has made a preliminary evaluation of by-product gypsum from the Chiyoda Thoroughbred 101 flue gas desulfurization process. The preliminary results were encouraging, but evaluation of larger samples is required. The sample tested was probably made from sulfur dioxide removed from flue gas of an oil-fired boiler or from tailgas of a Claus sulfur plant. By-product gypsum from flue gas of a coal-fired unit might contain impurities that would affect wallboard manufacture. This would have to be evaluated by the wallboard manufacturers.

Industry sources have indicated that limited expansion may occur at existing facilities, but that no new wallboard plants are anticipated in the immediate future.

Discussion of Available Gypsum Markets

There may be limited opportunity for utilities near existing wallboard plants in Ohio to sell by-product gypsum. The potential market is about 350,000 tons per year. The power plants located between Toledo and Cleveland appear to be best situated to sell by-product gypsum. Because they are located near calcining plants, transportation cost would be minimized. This does not necessarily mean gypsum manufacture is a practical alternative for these plants. Detailed venture analyses would be required to justify such a conclusion.

It remains to be demonstrated that the by-product gypsum is suitable for manufacture of wallboard in the United States. Furthermore, the current gypsum manufacturers may resist purchase of gypsum from the utilities because it would require that they shut down captive mines. Such details are best negotiated between the principal parties and are beyond the scope of this investigation.

Ammonium Sulfate

Applications

Essentially all of the ammonium sulfate consumed in the United States is used as fertilizer. Ammonium sulfate is used in fertilizers both as a source of nitrogen and as a source of sulfur. To date, sulfur has been an important consideration in fertilizer formulation in only a few areas of the United States, but if sulfur dioxide is removed from utility gases, then the soil in many areas of the United States may eventually become deficient in sulfur. At the present time, sulfur deficiencies are recognized in California and in portions of the southeastern United States. It is primarily in these areas where the consumption of sulfur-containing fertilizers (ammonium sulfate and normal superphosphate) is largest

Ammonium sulfate contains about 21 percent nitrogen, which is a relatively low analysis when compared with urea (46 percent) and ammonium nitrate (33.5 percent). The industry prefers to use the higher analysis fertilizers in order to minimize the transportation, storage, and handling costs per unit of nutrient. About half of the ammonium sulfate used as fertilizer is applied directly, the other half is used in the manufacture of granulated mixed fertilizer.

The physical form of a fertilizing material is important. Ammonium sulfate is recovered from most processes as rather fine crystals which have a tendency to create severe dusting problems. Such ammonium sulfate is not suitable for bulk blending operations. In recent years, the trend in the fertilizer industry has been towards increasing use of bulk blending to manufacture mixed fertilizers, with a corresponding

decline in granulation for the manufacture of mixed fertilizers. This decline in granulation plants is expected to continue. Because of this trend, the markets for ammonium sulfate in the northern farm areas are not expected to increase. TVA is currently looking into the development of mixtures of urea and ammonium sulfate fertilizers. Such fertilizers would be particularly useful in sulfur deficient soils. They would, however, probably be manufactured at urea plants located primarily on the Gulf Coast.

Supply

In the eastern United States, all of the ammonium sulfate produced is by-product material. Much of this by-product ammonium sulfate is derived from coke ovens. The manufacture of ammonium sulfate from coke oven gases has been practiced for several years by the steel companies as a means of limiting emissions to the atmosphere. The ammonium sulfate capacity from the steel companies in Ohio is estimated at over 95,000 tons per year, and in neighboring states this capacity is estimated at about 280,000 tons per year. Other sources of by-product ammonium sulfate include Standard Oil's acrylonitrile production plant at Lima, Ohio. Considerable by-product ammonium sulfate is also derived from caprolactam manufacture, but none of this is near Ohio.

In 1971, U.S. production of by-product ammonium sulfate from coke ovens was 539,000 tons and chemical by-product ammonium sulfate was 1,214,000 tons.* Production in Ohio and neighboring states is estimated at about 200,000 to 250,000 tons per year.

Consumption

In fiscal year 1972, the U.S. consumption of ammonium sulfate for direct application in fertilizer was about 2.1 million tons. About 45 percent is consumed in direct application and the remainder is consumed

* U.S. Bureau of Census, Current Industrial Reports, M28A(71)-14, Inorganic Chemicals, 1971, Washington, D.C. (1972).

in mixed fertilizers. Data are not readily available on the consumption of ammonium sulfate in mixed fertilizers by region. Nevertheless, it is estimated that the consumption of ammonium sulfate in mixed fertilizers in Ohio in fiscal 1972 did not exceed 48,000 tons. Ohio consumption of ammonium sulfate for direct application was 16,747 tons in fiscal 1972.* The consumption of ammonium sulfate for direct application in Ohio in fiscal 1972 was down from consumption of 22,657 tons in fiscal 1971. For the entire East North Central region in fiscal 1972, consumption of ammonium sulfate for direct application was 48,554 tons.

Much of the ammonium sulfate has been exported from the United States, primarily under AID-financed programs. Thus the overall marketability of ammonium sulfate has in the past depended to a large extent upon export markets and especially on Government-subsidized sales in export markets. Ohio utilities are not well located to participate in these export markets.

Discussion of Ammonium Sulfate Markets

It appears that the demand for ammonium sulfate in and near Ohio is more than adequately supplied by by-product material made in Ohio and neighboring states. Furthermore, unless Ohio soils become sulfur deficient as a result of removal of sulfur dioxide from utility flue gas, ammonium sulfate will remain a rather undesirable fertilizer material. Finally, even without competition from other by-product ammonium sulfate made in the area, the entire Ohio 1972 consumption could have been supplied by one 200 to 250-mw generation station.

It does not appear practical at present to market large amounts of ammonium sulfate from Ohio utilities. However, there is some possibility of "no-cost" disposal of limited amounts by export firms involved in the international fertilizer market. The marketing of ammonium sulfate in the rice growing regions of Texas, California, and some other Western states will not be profitable, but might be preferable to the costs of operating a throw-away emission control process.

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* U.S. Department of Agriculture, Consumption of Commercial Fertilizers for fiscal year ended June 30, 1972, Washington, D.C. (May, 1973).

Sodium Sulfite

Although it would be relatively easy to absorb sulfur dioxide from flue gases in a caustic solution to manufacture sodium sulfite, the market for this chemical is limited. In 1971, the total U.S. production of sodium sulfite was 204,000 tons.* Between 1967 and 1971, the market fluctuated between this low figure and a high of 250,000 tons. A modest growth rate of about 3 percent per year through 1976 has been projected.**

The paper industry is the major consumer of sodium sulfite. An estimated 80 percent of the sodium sulfite is used in the neutral sulfite semi-chemical pulping process. The remainder is consumed in water treatment, photography, and miscellaneous applications. Many paper mills have captive sodium sulfite capacity, but some of these are expected to return to purchasing the chemical in the merchant market. Captive capacity of paper mills has been estimated at 500,000 tons, compared with total merchant capacity of 267,000 tons. In the Ohio region, most of the sodium sulfite is supplied either from the Koppers plant in Petrolia, Pennsylvania or by Reichhold from their Tuscaloosa, Alabama plant.

There are two pulp mills in Ohio using the neutral sulfite, semi-chemical process. Container Corporation in Circleville purchases sodium sulfite. The other sulfite pulp mill, owned by Stone Container Corporation in Coshocton, is currently testing a new pulping process which does not use sulfur compounds. If they were to convert back to the sulfite process, the total market for sodium sulfite in Ohio would probably be less than 25,000 tons per year. Even if the markets at sulfite mills in western Pennsylvania, Indiana, and Kentucky could be penetrated, this would increase the market by only an estimated 35,000 tons annually.

Another factor which should be considered is that paper mills in the midwestern United States generally burn high-sulfur coal to generate steam for their operations. If emission controls are applied to these industrial

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* U.S. Department of Commerce, Current Industrial Reports, Inorganic Chemicals, 1971, Series M28A (71)-14, Table 4 (October, 1972).

** Chemical Marketing Reporter, 201, 9 (April 10, 1972).

boilers, it is likely that they would recover the sulfur in a form which could be used in their operations.

It appears that the sodium sulfite market is currently too small to provide a practical outlet for sulfur recovered from utility flue gas. This market is apt to shrink if sulfur emission controls are enforced against owners of industrial boilers.

The potential market for sodium sulfite is insignificant compared to the quantities of sulfur emitted by even a small (200 MW) utility plant.

Sulfur Dioxide

Although several of the flue-gas desulfurization processes concentrate the sulfur dioxide present in the flue gas as a part of the recovery process, no process is designed specifically to recover liquid sulfur dioxide by purification and compression. It is not feasible to ship sulfur dioxide in the gaseous form and, therefore, the entire merchant market for sulfur dioxide is for the liquid.

Although growing, the markets for sulfur dioxide itself are small and diverse. The reported U.S. capacity for sulfur dioxide is 154,000 tons.* 1971 production of sulfur dioxide was 95,414 tons.** During the period between 1967 and 1971, shipments of sulfur dioxide have fluctuated between 83,000 and 101,000 tons. Thus, it appears that a small generation station with a capacity of 500 to 550 MW could supply the present United States requirements for merchant sulfur dioxide.

Because of the fluctuations in demand for sulfur dioxide, the need to store it under pressure, and the expense of shipping it to distant locations throughout the country, production of such large quantities might not be practical. The manufacture of sulfur dioxide from elemental sulfur provides considerable flexibility, since production can be easily adjusted to fit demand.

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* Stanford Research Institute, 1973 Directory of Chemical Producers.

** U.S. Bureau of Census, Current Industrial Reports Series M2A (71)-14, "Inorganic Chemicals", 1971, Washington, D. C. (1972), p 14.

Manufacture of liquid sulfur dioxide does not appear at present to be a practical alternative for most Ohio utilities. However, a detailed cost analysis of the transportation cost of SO_2 versus the cost of converting SO_2 to sulfur, transporting the solid, and then reoxidizing to SO_2 and finally to SO_3 seems warranted at this time.

MARKETING PRACTICE FOR BY-PRODUCT SULFUR COMPOUNDS

Utilities Experience in the United States

The electric utilities in the United States have had no substantial experience in marketing chemicals. A few utilities do attempt to market flyash which is recovered as a by-product from the generation of electricity. Many others, however, either discard the flyash or attempt to sell by-product flyash through brokers. As a general rule, the utilities have not yet developed the marketing experience and the distribution channels to sell the by-product sulfur compounds which might be recovered from flue-gas desulfurization processes. Many also recognize that diversification into an unfamiliar area like chemicals would require a major commitment of management effort. Therefore, the practice for marketing by-product sulfur compounds has been for the electric utility to market through an established chemical company.

Although the arrangements for marketing by-product sulfur compounds are made directly between the utility and the chemical company, the vendor of the flue-gas desulfurization equipment is usually instrumental in bringing these parties together. In fact, this service on the part of the vendor is an integral part of the sales effort.

Some specific examples of the experience in marketing by-product sulfur compounds from utility flue gas are described below.

Illinois Power

A demonstration unit for the Monsanto Cat-Ox process has been installed at the Wood River Station of Illinois Power. Although there have been several operating problems with this process at Wood River, Monsanto estimates that approximately 70 tons sulfuric acid will be produced per day once operating problems have been solved.

Monsanto has agreed to market all sulfuric acid produced at the Wood River demonstration plant. This marketing arrangement is in the form of a 5-year contract with provisions for renewal. The net revenues are split with 75 percent to Illinois Power and 25 percent to Monsanto. Monsanto would expect to offer their marketing expertise to other utilities purchasing a Cat-Ox system. Therefore, Monsanto would make a market survey to ensure the acid could be sold before recommending Cat-Ox at any specific location.

Boston Edison and Potomac Electric Power

The first prototype of the Chemico/Basic magnesia scrubbing process was installed on an oil-fired boiler at Boston Edison's Mystic Station. The flue gas from a 150-MW unit is treated with magnesia, and the sulfur is removed in the form of hydrated magnesium sulfite. This magnesium sulfite is dried to remove free water and the water of hydration. The magnesium sulfite is then transported by truck to the Essex Chemical sulfuric acid plant at Rumford, Rhode Island, where sulfur dioxide is regenerated and made into sulfuric acid. Magnesia regenerated at the same time as sulfur dioxide is returned to Boston Edison. Although there were some start-up difficulties with this process, it was reported on stream in July, 1973, and operating at 85 percent availability.

The current operation at Boston Edison is a pilot demonstration of the process and cannot be considered a typical commercial operation. The Essex Chemical sulfuric acid plant at Rumford is very small, old, and had been scheduled for shutdown. The plant was originally built in 1926 and has a rated capacity of 50 tons per day. Arrangements were made to add a calcining unit to process the magnesium salts and to continue operation

of this sulfuric acid plant for the duration of the testing of the Mystic prototype installation. A second Chemico unit using the magnesia scrubbing process is currently being installed at Potomac Electric Power Company's Dickerson Station. Half of the flue gas from the Dickerson #3 unit will be treated, and the magnesium sulfite will also be shipped to Rumford for conversion to sulfuric acid. The Dickerson #3 boiler is a coal-fired unit rated at 190 MW. Upon completion of these two demonstrations, the Rumford acid plant will be closed.

Of commercial significance would be the marketing of magnesium sulfite or sulfuric acid from the #4, #5, #6, and #7 units at the Mystic Station. The first three are each 150 MW and #7 is a new 600-MW unit. This project is still in the planning phase. Negotiations are currently underway between Boston Edison and several acid companies operating within shipping distance of the Mystic Station*. Boston Edison expects to decide whether to install additional scrubbing units or to burn low-sulfur fuel oil at these units by October 1, 1973. Since the possible marketing arrangements are still in the negotiation stage, no information is available on marketing sulfuric acid from the commercial installation at this time. Chemico is participating in the negotiations and is deeply involved in identifying potential customers for the sulfur dioxide.

Philadelphia Electric

Philadelphia Electric Company is installing a prototype sulfur dioxide removal system on its coal-fired Eddystone #1 unit. The Eddystone #1 prototype will handle flue gas from the equivalent of 120 MW. It is the only recovery scrubbing system in the United States which is entirely funded by the utility with no EPA or other governmental monies are involved.

The Eddystone prototype is a magnesia scrubbing system designed by United Engineering & Constructors, Inc. In addition to the design and engineering, United Engineers was instrumental in locating a customer for

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* The logical candidate appears to be Monsanto at Everett, Mass. The Mystic Station is also in Everett and is near the Monsanto plant.

the sulfur dioxide to be regenerated. Although United Engineers assisted in the arrangements for marketing the by-product, the final negotiations were made directly by Philadelphia Electric. There were several potential customers in the Philadelphia area. With the assistance of United Engineers, Philadelphia Electric has reached an agreement with Olin Corporation who will take the regenerated sulfur dioxide at its Paulsboro, New Jersey sulfuric acid plant.

Sulfur dioxide will be removed from the flue gas at the Eddystone #1 station in Philadelphia. The sulfur removed at this location exits from the process in the form of dry magnesium sulfite. The magnesium sulfite will then be transported by truck to Olin's sulfuric acid plant which is about 20 miles from the power generation station by road. It is expected that a round trip by truck will take about 1.5 hours. The transportation cost has not yet been determined.

At Paulsboro, the magnesium sulfite will be processed to regenerate magnesia and a gas containing about 17 percent sulfur dioxide. The magnesia will be returned to Eddystone for reuse in scrubbing. The sulfur dioxide will be sent to the contact sulfuric acid plant. The regeneration unit which converts the magnesium sulfite to sulfur dioxide will be owned by Philadelphia Electric, although it will be located at Olin's site and will be operated by Olin. The magnesium containing salts will be owned by Philadelphia Electric throughout, and title to the sulfur dioxide will be transferred at the regeneration unit.

The Olin sulfuric acid plant in Paulsboro currently burns elemental sulfur and reprocesses acid sludge to manufacture sulfuric acid. Sulfur dioxide from the Philadelphia Electric prototype unit will constitute only a small portion of its feed. Both Philadelphia Electric and Olin regard this as a research project.

Neither Philadelphia Electric nor United Engineers believe that it would be feasible to ship large quantities of magnesium sulfite from treating all flue gas of a typical power plant to a sulfuric acid plant. Rather, they believe that the sulfuric acid plant should be constructed at the electric generation station.

Northern Indiana Public Service

Northern Indiana Public Service Company (NIPSCO) is currently installing a Davy Powergas/Allied Chemical demonstration unit to desulfurize flue gas at the Mitchell station. The Davy Powergas technology will be used to recover and concentrate sulfur dioxide, and the Allied Chemical system will produce elemental sulfur. The project is funded by EPA.

Allied Chemical will have a management contract to operate both the Davy Powergas unit and the Allied reduction unit. Allied will also market the by-product sulfur and any sodium sulfate obtained from the Davy Powergas unit. The proceeds from the sale of the chemical will revert to NIPSCO.

Allied considers its arrangement with NIPSCO as fairly typical of the manner that they would approach the sale of sulfur from installation of any other Allied process units. The Allied reduction technology can be applied to any scrubbing technology which regenerates concentrated sulfur dioxide, and is not necessarily limited to use in conjunction with the Davy Powergas system. Allied prefers long-term contracts for the life of the scrubbing unit for such arrangements. A possible alternative would be 5-year renewable contracts.

Markets in Japan for By-Product Sulfur *

Atmospheric emission of sulfur dioxide is under national control in Japan with progressive increasing limitations on emissions. Controls are based on ambient standards of SO_2 concentrations that are to be achieved by 1978. These standards are to be met by three simultaneous

*This section on Japanese markets is adapted from two reports:

a. Elder, H. W., Princiotta, F. T., Hollinden, G. A., and Gage, S. T., "Sulfur Oxide Control Technology. Visits in Japan-August, 1972", Interagency Tech. Committee, Division of Chemical Development, Tennessee Valley Authority, Muscle Shoals, Alabama (October 30, 1972).

b. Ando, Jumpei, "Utilizing and Dispusing of Sulfur Products from Flue Gas Desulfurization Processes in Japan", Special Reports to Control Systems Division, Environmental Protection Agency, Research Triangle Park, North Carolina (May, 1973).

programs: (1) to desulfurize residual oil remaining after distillation of volatile portions, (2) to import low-sulfur crude oil, and (3) to remove SO_2 from flue gases. The recovery of sulfur by-products in the past has been prompted by the limited supply of Japanese sulfur and the consequent cost advantage over products based on imported sulfur.

Sulfur products which have been successfully marketed in Japan include elemental sulfur, sodium sulfite, sodium sulfate, sulfuric acid, and calcium sulfate (gypsum). Because of oversupply, ammonium sulfate is no longer marketed but is discarded by three plants still producing it.

Installations for Recovery of By-Product Sulfur

Japan is in a period of transition from sulfur recovery for marketing of by-products to the installation of additional units primarily directed to controlling emissions. For these latter units, there is no assured market; especially so, because the capacity for recovered sulfur is expected to grow extremely rapidly. For example, nine major power companies producing 70 percent of Japan's electrical power are turning to flue gas desulfurization very strongly as the limitations on sulfur emissions become more stringent. Desulfurization systems had been installed for flue gas treatment in power plants with a total capacity of 357 MW in 1972, and new installations are expected to increase the total capacities to 2,700 MW in 1974 and 4,800 MW in 1976. The 13-fold increase projected for a 4-year period includes various methods of flue-gas treatment which produce both throw-away materials and useful by-products.

In the past, installations in Japan for sulfur recovery were justified largely by their yield of salable products. Now, there is more similarity in the situation for sulfur recovery and marketing between the Ohio utilities and the Japanese marketing experience:

(1) New installations will be facing a relatively saturated market for sulfur products in both places, and will be competing on the basis of price rather than profitability.

(2) A very low proportion of the electrical generating capacity is currently treated for flue gas desulfurization. Even with planned installations, only about 10 percent of

electrical generating capacity in Japan will be treating flue gas in 1976.

(3) The total area covered by the industrialized regions of Japan's main island of Honshu is not far different from the total area of the Air Quality Control Regions wholly and partially in Ohio. These areas are both served by water transportation; Ohio has the Ohio River and the Lake Erie ports, while Honshu is an island between the Sea of Japan and the Pacific Ocean.

(4) The total annual emissions of SO_2 in the two regions are similar. About 6 million tons of SO_2 was emitted in Honshu in 1971 while burning heavy oil, which is the chief source of SO_2 in the atmosphere. In the same year, it is estimated that the total utility SO_2 in the Air Quality Control Regions of Ohio was about 4 million tons.

There are three significant differences that impinge upon this study of by-products:

(1) Many sulfur chemicals have a higher value in Japan than in the United States. The greatest price differential is for gypsum.

(2) Honshu has a population of six to eight times that of Ohio, so that the efforts to find valuable by-products markets to support the denser population were started earlier and explored in more detail. Thus, the experience may be helpful to Ohio utilities now faced with a similar necessity.

(3) Much of the fuel for power generation is heavy fuel oil rather than coal as in Ohio. Both have high sulfur content of the order of 4 percent, but the impurities introduced into by-products may be lower from oil-derived particulate matter than from fly-ash in the flue gases from coal.

Elemental Sulfur. By-product elemental sulfur is produced primarily in Japan by removing sulfur from heavy fuel oil before it is burned. About one-fourth of the total heavy oil was desulfurized in 1971, giving 256,000 long tons of sulfur as a by-product. Additionally, by-product sulfur from other sources, such as oil refining, increased the supplies to the point where recovered sulfur represented 90 percent of the total in 1971 and 97 percent of the total elemental sulfur in 1972.

Elemental sulfur has two advantages with the oversupply of sulfur that is in prospect in Japan. If it is not salable, it can be stored indefinitely for eventual recovery. This would be an alternative to finding immediate markets, even though the prospective need for its recovery is not certain. It occupies the smallest volume and requires the least transportation and storage space. The second advantage is that it can serve as a starting point for any of the other sulfur compounds that may find use in the future. The route to sulfuric acid, for example, is by way of combustion of the sulfur with air to sulfur dioxide, and then the manufacturing process proceeds from there.

Sulfuric Acid. Sulfuric acid is the most important acid for industrial uses in Japan as it is in the United States. Various processes have been and are being installed for sulfur recovery from waste gases which give sulfuric acid as the marketable end product. In 1972, the total sulfuric acid production was over 7 million tons of which almost 60 percent was by-product acid produced from the sulfur dioxide recovered from smelter off-gases. Only 4 percent was made by burning of elemental sulfur to sulfur dioxide, and the remainder was from roasting of pyrite. It appears that Japanese industry has no unique processes or marketing procedures for sulfuric acid that are not already available to the United States. It is possible that the prospective increase in recovery of sulfur dioxide from industrial waste gases will continue to cause the reduction of use of pyrite for sulfuric acid. However, pyrite is more easily stored to meet fluctuating markets for sulfuric acid than is sulfuric acid produced from recovered SO_2.

Sodium Sulfite. One widely used paper-making process consumes sodium sulfite in the preparation of paper pulp from raw wood. Since sodium sulfite solution is the absorptive agent for sulfur dioxide in major processes for flue-gas clean-up, as already discussed, and more is formed during absorption, this surplus amount represents a significant direct outlet for the by-product sulfur as an alternative to regeneration for recovery of SO_2. In the 5-year period from 1967 to 1971, in Japan, the production of sodium sulfite tripled to reach 330,000 tons of anhydrous material, most of which presumably went into paper making. However, the sale price also started to decrease as a result of oversupply, and the future demand is definitely limited.

Sodium sulfite recovery differs in the final treatment of the absorbing solution from the process for recovering sulfur dioxide. During absorption, sulfur dioxide combines with sodium sulfite to form sodium bisulfite. Then this product is converted to sodium sulfite by neutralization with the alkali, sodium hydroxide. One-half of the resulting sodium sulfite solution is recycled to be used as absorbent, and the other half is evaporated to form crystalline solid sodium sulfite for sale.

Calcium Sulfate (Gypsum) and Calcium Sulfite. According to Ando*, gypsum is the preferred by-product in Japan. It has two major uses there: (1) for retarding the rate of setting of Portland cement, and (2) as the major component for certain types of wall tile, wallboard, lath, and various kinds of plasters. The demand for gypsum in Japan is projected to increase by about 50 percent between 1970 and 1976. In 1970, the demand and supply were balanced at about 4,000,000 tons.

There are two important sources of by-product gypsum, of which the earlier one is gypsum recovered from the manufacture of superphosphate fertilizer from phosphate rock. The other major source is from recovered sulfur, which is expected to supply a large part of the projected increase in demand, because of increased recovery of sulfur values to reduce emissions. Furthermore, gypsum is reputedly more desirable for landfill than calcium sulfite if it must be disposed of because of lack of markets. It is claimed to be more easily dewatered than calcium sulfite to form a stable fill that is relatively inert and innocuous.

*Reference page 60.

Some tests have already been made in Japan by Mitsui Aluminum Company, which has produced wallboard from by-product calcium sulfite recovered by treating coal-fired flue gas with the Chemico-Mitsui process. Gypsum is produced from the calcium sulfite by oxidation. The gypsum contains slightly more than 10 percent impurities, including fly ash and other materials. It is expected that the strength of the wallboard manufactured from this typsum will be up to required specifications. Plans are being made for an industrial scale operation to produce wallboard from this by-product process in 1974.

Ammonium Sulfate. Ammonium sulfate is a by-product of scrubbing the flue gases with ammonia solution. It has been produced in several ammonia scrubbing plants but is not a saleable product in the present markets open to the Japanese. One plant producing solid ammonium sulfate is converting that product into gypsum, which can be sold in Japan. This is not a feasible alternative in the United States.

By-Product Specialties. The prospect of market saturation for by-product sulfur induces close attention to any prospect for developing new specialty products that can be protected by patents, and thus create new and profitable markets. Until patents are published, development work is usually highly proprietary. One patent has recently been issued* describing the precipitation of calcium sulfite in a form useful as a filler for plastics. Control of the conditions of precipitation undoubtedly permits better control of surface properties, hydration, crystal shape, and particle size so as to impart desirable characteristics to the filler. It has been noted earlier that calcium sulfite is less desirable than calcium sulfate as a landfill, because the sulfite has a smaller particle size, which makes it difficult to handle. This process presumably takes advantage of the controllable properties of calcium sulfite that are favorable to superior performance as a filler for plastic materials.

*U. S. Patent 3,739,060, "Method of Preparing Calcium Sulfite for Use as a Filter for Plastics", assigned to Lion Fat and Oil Company Limited, Tokyo, Japan (June 12, 1973).

There have also been announcements this year of other new materials already in trial production. One is a gypsum-polymer composite, which is indicated to be a filled plastic suitable for severe duty construction use that requires more resistance to abuse than wallboard. A synthetic paper is a heavily loaded plastic film containing about 70 percent of specially prepared calcium sulfite. It was announced that this paper could command a premium price because of superior properties.

Significance of Japanese Experience for Ohio Utilities

Japanese industry, when faced with the necessity for reducing sulfur emissions by removing and perhaps recovering sulfur for reuse, has attempted to solve problems very similar to those facing the Ohio utilities. It appears that these attempts have been pointed toward three activities. First, installations have been made to produce materials for present markets, when an expanding market was predictable, and the competitive sources of supply did not have an overwhelming advantage. This appears to have been the situation that prompted the expansion in production of gypsum as a by-product. Both major uses, for wallboard and as a concrete additive, required substantial amounts of gypsum and these industries were expanding. Major competition came from gypsum recovered by a fertilizer industry, which presumably was already better established and did not have the same incentive to expand as other industries.

Second, Japanese industries seek flexibility of the process to permit several by-products, if possible. A Battelle representative who visited Japanese installations in July, 1973, reported three plants with oil-fired boilers had installed the Chiyoda process, two of which were operating and one under construction. This process washes the flue gases with slightly acidified water to absorb SO_2. The concentration of the collected washings is about 4 percent acid. These are partially neutralized with limestone to convert the acid to gypsum of commercial quality. Gypsum is also the preferred low-cost throwaway product in Japan, which permits some versatility in the operation.

Elemental sulfur also is viewed favorably for Japanese plants because it can be stored indefinitely at least expense, and then supplied

as the feed for any process to make sulfur-containing materials, when the market is favorable. However, it would not be selected initially unless there were already a fluctuating demand for sulfur and only a periodic oversupply.

Third, the Japanese are searching for new uses for sulfur by-products that may reach a substantial volume of production. These include other construction materials in addition to wallboard, and fillers for plastics and synthetic paper as already described.

Sulfur Recovery from Fossil Fuel Processing

Producers of the three classes of fossil fuels, natural gas, petroleum, and coke, have a significant technological advantage over Ohio utilities when they are required to limit sulfur emissions. Whereas the utilities must handle sulfur dioxide in flue gases, the fuel producers have available to them a more attractive side stream of surplus hydrogen sulfide which is separated from their primary products during the purification treatments. Hydrogen sulfide is itself also a fuel that can be used for energy production by combustion; the side stream is much more concentrated in hydrogen sulfide than are the flue gases of the utilities in sulfur dioxide; and the hydrogen sulfide is a reducing agent for production of elemental sulfur from sulfur dioxide. Thus these producers have a number of options for recovering costs and perhaps profiting from their sulfur-containing impurities. If there is a market for sulfur they can burn one-third of their supply of hydrogen sulfide in air and combine the combustion product sulfur dioxide with the remaining unburned hydrogen sulfide to produce sulfur. If there is no market for sulfur this solid product can be stored or disposed of at minimum cost, as noted previously. Generally speaking, capital costs are relatively low, and no significant inputs of energy or additional materials are required. If a market exists for sulfuric acid, the by-product stream of hydrogen sulfide can be burned completely to sulfur dioxide with air and the combustion products can be sent to a sulfuric acid plant.

The competitive advantages of having several alternatives can only be met by finding superior marketing arrangements for the Ohio utilities, on the basis of preferred location relative to market, or special situations.

Natural Gas Producers

Many natural gas wells contain hydrogen sulfide as one component of the gas mixture. This must be removed because of the corrosive nature of the sulfur dioxide produced when it is burned. Substantial amounts of elemental sulfur were produced in 1970 from natural gas, with Texas accounting for about 75 percent of the total production. There is also a large amount of sour gas treated from the fields of Alberta, Canada, with recovery and storage for marketing of high tonnages of elemental sufur. These two regions represent the major sources of competition for sulfur by-product markets of the Ohio utilities.

Petroleum Refining

The locations of petroleum refiners are much more widely scattered than are the gas fields with high hydrogen-sulfide content. Thus, by-products from petroleum refiners will tend to supply local or regional markets first and will not block out from consideration large areas of potential markets for Ohio utilities' sulfur. However, the petroleum refiners have the same technological advantage as the natural gas producers, because they, too, start with hydrogen sulfide in their by-product stream. Here, too, the Ohio utilities cannot compete technologically, and their markets are local or require special situations.

Coke Production

By-product coke ovens have usually recovered only liquid products for sale and have used the combustible off-gases as process fuel. These off-gases included a substantial amount of hydrogen sulfide which was discharged to the atmosphere as its combustion product sulfur dioxide. Increased attention to pollution controls on coke oven installations has

prompted recovery procedures to separate hydrogen sulfide before the off-gases are burned. One example is the Clairton works of United States Steel, which has had hydrogen sulfide recovery as a control measure for several years. This hydrogen sulfide stream is converted to elemental sulfur.

It is probable that sulfur products from coke ovens will have some impact on the marketability of sulfur products within the areas otherwise available to Ohio utilities. This example is cited to show that pressure for antipollution controls on all industries with sulfur emissions will favor the growth of available sulfur supplies and incidence of surpluses as control measures are implemented.

Development of Technology and Markets by Smelters

Technology of Ore Smelting

The nonferrous smelters recover copper, lead, and zinc metals from their sulfide ores by stepwise processing with heat and fluxes to form a melt of crude metal and slag, which separates into layers. The bottom layer of metal is withdrawn for further refining, and the nonmetallic slag is discarded. The off-gases from the processing steps carry sulfur dioxide derived from the sulfide portion of the ore. In general, the sulfur dioxide concentration in smelter off-gases is substantially higher than can be expected in the flue gas from combustion of high-sulfur coal by the Ohio utilities. Recovery costs are correspondingly lower, and some smelters have found it profitable for many years to sell by-product acid manufactured from the recovered SO_2.

The smelting of nonferrous ore usually starts with a roasting step, in which ore concentrate is heated in the presence of air. A part of the iron sulfide also present in the concentrate is converted to elemental iron plus sulfur dioxide in the off-gases. These contain about 2 to 6 percent SO_2 when a multiple hearth roaster is used. Optimum sulfur dioxide concentration for sulfuric acid manufacture is 8 percent or above, but these gases could be processed directly in a sulfuric acid plant after cleaning and cooling. An

alternative roaster uses a fluidized bed in which fine ore particles are partially suspended and violently mixed in a heated, upward-flowing air stream that balances the tendency of the particles to fall by gravity. Because of the better efficiency of mixing and contact between air and ore in the fluidized bed, less air needs to be used, and SO_2 in the off-gases may have concentrations of about 12 percent. Fluidized beds have been used most commonly for lead or zinc ore, although copper smelters may be prompted to turn more to this method in the future in an effort to lower costs while meeting antipollution regulations.

The next step in treatment of copper ore feeds the roasted ore into a reverberatory furnace together with a solid flux in a mixture that is melted on the floor of the furnace by radiated heat from the flame above the surface and from reflections off the hot roof of the chamber. When the flux reacts with the roasted ore a metallic phase is set free that settles to the bottom of the pool as a denser liquid layer with the lighter molten slag floating on top. Each layer is withdrawn periodically from its own tap hole at the appropriate level in the furnace wall or bottom. In this step of the process about 10 to 20 percent of the sulfur content of the charge to the furnace is given off as sulfur dioxide mixed with the effluent combustion gases. These gases contain less than one percent sulfur dioxide, and normal practice has been to release them up the stack. However, the sulfur dioxide concentration is higher than the 0.2 to 0.3 percent SO_2 expected from the combustion of high-sulfur coal, and these gases will have to be treated.

It is not certain what the smelting industry will do to clean up the gases from the reverberatory furnace to meet the limitations on source emissions. There are two alternatives that have been used by foreign smelters. Each of these gives off gases with higher sulfur dioxide concentration that is more adaptable to by-product SO_2 recovery and sulfuric acid manufacture. The electric furnace for copper smelting uses electrodes immersed in the slag layer, which acts as the heat generator where current is passed through it to the lower metallic layer as the opposing electrode. The total volume of SO_2 liberated is about the same as from the reverberatory furnace, but there are no gases produced by combustion of fuel, so that a concentration of about 3 percent SO_2 can be attained. This process is economically feasible only where low-cost electric power is available.

Flash smelting furnaces have also been developed in which the ore concentrates in the form of small particles are smelted directly without a preceding roasting step. The particles can be burned by predrying the ore concentrate powder and using preheated air in a manner similar to the burning of pulverized coal suspended in air. The flux is also introduced in powder form together with the predried concentrates of ore, so that the smelting reactions take place in suspension and after they settle to the furnace floor until the separate layers of molten metal and slag are formed. About 14 percent SO_2 gas concentration can be reached in this furnace using preheated air.

If pure oxygen is available at low cost it can be used in a similar flash smelting furnace to burn flotation concentrates in the presence of powdered flux. In this modification there is no dilution of the off-gases by atmospheric nitrogen, so that concentration of SO_2 can be as high as 80 percent. This alternative opens a wider market, because pure SO_2 can be recovered for sale as a liquid.

The metal layer tapped from the smelting furnace contains about 30 percent copper, 40 percent iron, and 26 percent sulfur. This copper matte is transferred to a converter with more flux added to combine with the iron while air is blown through the mixture from below the liquid surface. Most of the iron combines with the flux in the top layer during blowing, and is skimmed off for discard. The remaining layer of molten metal still contains about 24 percent sulfur, which is oxidized to SO_2 in the exhaust gases by continuing the blowing with air. When blowing is completed the copper layer is about 99 percent pure. The off-gases from the conversion step commonly contain 2 to 6 percent SO_2, because the converter exhausts into an open hood and surrounding air is drawn into the hood to dilute the rising hot gas. By special designs to reduce this air infiltration the SO_2 concentrations can be increased to more than 6 percent minimum.

This description of smelting steps shows that there are a number of options available in each step to improve the traditional methods for recovering sulfur dioxide by increasing the concentration of this gas in the off-gas mixture. The trend is to exercise these options whenever new installations are required to meet emission standards. Therefore, the amounts of recovered sulfur dioxide will presumably increase in the nonferrous metal smelting industry.

This industry is in a position similar to that of the Ohio utilities in the sense that it, too, is limited to the recovery of sulfur dioxide. Unlike the processors of fossil fuels discussed in the preceding section, there is as yet no easy route to hydrogen sulfide and from there to elemental sulfur. However, the smelting industry has the inherent advantage of reasonable options for increasing the concentrations of sulfur dioxide in their off-gases, which is not available to the Ohio utilities except to a limited degree by burning coal with higher sulfur content. Therefore, the smelters can treat lesser quantities of gaseous emissions with lower costs for the same amount of recovered SO_2. Their competitive advantages can only be met by superior marketing arrangements by the Ohio utilities, on the basis of location of each utility or some other special market situation.

Smelter Marketing Experience

Eastern United States. Many of the metals companies which operate smelters prefer not to market by-product acid or other chemicals. Many smelters, therefore, have contracts with chemical companies to market by-product sulfuric acid generated at the smelters. A typical contract would require the chemical company to take all sulfuric acid produced at a smelter at a price, f.o.b. smelter, which would be adjusted for fluctuations in sulfur prices and possibly in labor rates. Most contracts have automatic annual renewal clauses, with a 2-year notice required by either party to terminate the contract.

There are currently three smelters in the Eastern United States producing by-product acid which would be potentially in competition with acid from Ohio utilities. These are the St. Joe Minerals zinc smelter at Monaca, Pennsylvania, the American Smelting and Refining (Asarco) zinc oxide plant at Columbus, Ohio, and the Cities Service smelter at Copper Hill, Tennessee.

Of these three, St. Joe Minerals sells their acid to Allied Chemical, f.o.b. smelter. Allied then markets the acid to end users. Allied frequently cuts back production at its own sulfuric acid plants in the Ohio Valley in order to accommodate this by-product acid.

Asarco, on the other hand, markets their own acid from the Columbus plant; Asarco does sell acid to chemical companies at other locations. Cities Service markets acid from the Copper Hill smelter directly to the end-user.

Canadian Successes. One of the best examples of what can be done by industry under proper incentive is provided by the Consolidated Mining and Smelting Company of Canada, Ltd. (Cominco) plant at Trail, British Columbia. The Trail plant of Cominco was started many years ago to treat gold mine wastes (primarily a copper ore) from the Rossland mine. It now recovers lead, zinc, silver, and a few more minor minerals from the Sullivan mine at Kimberly, British Columbia, which is about 200 miles north of Trail.

In the late 1920's, Stevens County in the State of Washington filed a suit which cited the company for the pollution being emitted by the Trail smelter and case was eventually decided by the World Court. In essence, the Court ruled that the Trail plant, which is located about 8 miles north of the U.S.-Canadian border, would have to clean up its smelter and sinter plant stack gases, which ran as high as 8 percent SO_2. Trail is a village in an extremely deep canyon of the Columbia River, and the mountains tower above the stacks.

Cominco eventually developed a remarkably versatile ammonia scrubbing system. All the off-gas from the sinter plant at Trail is washed with ammonia solution. This stream represents 180 t/day of sulfur at a concentration of 1.5 percent SO_2, and roughly 60 percent is recovered. The off-gas from the zinc roasters is split into two streams. Roughly 580 t/day of sulfur is in zinc ore and about 10 percent of this is absorbed in ammonia solution. The bulk of the SO_2 (at 8.5 percent conc.) goes to catalytic oxidizers to burn the SO_2 to SO_3 and produce about 1600 t/day of sulfuric acid in three separate acid plants of varying vintage. Some of the acid is used to react with the ammonium bisulfate solution from the scrubbers to produce SO_2, which is compressed to liquid and sold at the rate of 120 t/day. At the present time the plant cannot produce enough SO_2 to meet demand.

The sulfur output of the plant breaks down roughly as follows - about 5/8 of the sulfur is sold as sulfuric acid, 1/4 as SO_2, and 1/8 as ammonium sulfate. SO_2 is sold as far away as Glen Falls, N.Y.; Hobbs, N.M.; Los Angeles; and Alaska. The SO_2 market was initially quite small, but Cominco takes some credit for its expansion. SO_2 normally is used for bleaching dried fruit and in sugar beet production. However San Francisco buys 200 t/year as a chlorine scavenger to clean up excess chlorine after waste treatments. The use in Los Angeles is for oxygen scavenging to clean up water before compression to flood oil wells. It is used in Manitoba for pH control by a mining firm. Some SO_2 is also used in the manufacture or use of chlorine dioxide and zinc and sodium hydrosulfites, all of which are important in the paper industry (although the use of zinc hydrosulfite is declining because of environmental considerations).

Cominco is the second largest SO_2 producer (65,000 t/year) in Canada. The largest is Chemical Industries at Sudbury, Ontario (95,000 year), which until recently sold most of the product to an adjacent pulp mill (the mill recently shut down). Virginia Chemicals and Essex are the biggest SO_2 producers in the United States.

Cominco sells most of its sulfuric acid on the West Coast. However, substantial amounts are also sold in Calgary, despite the fact that sulfur recovered from natural gas is available there in tremendous quantities. For many years ammonium sulfate was a major product and was shipped to China for use as fertilizer.

The only serious plant problem still unsolved in the white plume which consists of ammonium sulfate. Only about 2 tons/day of ammonium sulfate goes up the stack with about 1 ton/hr of unreacted SO_2, but the crystals are extremely visible. A pilot mist eliminator is currently being tested and appears promising. The SO_2 levels have now been reduced to about 1000 ppm, but this, of course, is too high a level for untreated utility stack gases in the United States. The ammonium sulfate is considered by Cominco to be harmless and the plant makes much use of attractive flowers and shrubs on their grounds to show evidence of this .

The plant represents a good example of practical environmental engineering. Although the process in the past has been considered to be too expensive for use with utility stacks, this view may change as a result of difficulties with the other alternatives open to utilities.

CONCLUSIONS AND RECOMMENDATIONS

(1) The major outlet for sulfur by-products from all the Ohio utilities probably would be in the Gulf Coast for phosphate fertilizer production. A detailed study of the net process energy and cost requirements for production of sulfur, sulfur dioxide, and/or sulfuric acid in Ohio and shipment and use in Florida and other southern states as sulfuric acid is needed to determine at what price the Ohio utilities can compete in this market.

(2) An alternative scheme to locate at least one phosphate fertilizer plant in Ohio is conceptually promising and should be evaluated in detail. Such a facility might supply the sulfur outlet necessary for several of Ohio's major utility plants.

(3) The nearby surrounding states offer some market potential for Ohio utilities, but because of similar utility emissions, and possibly similar regulations in some states, the additional markets available to Ohio utilities is probably not large. Those Ohio utilities that are somewhat slow to react to the sulfur disposal problem will be forced to compete in this somewhat limited and transportation cost-sensitive market.

(4) There may be a very substantial excess of sulfur as emissions from Ohio utilities over the Ohio market needs for sulfur. Those utilities that act rapidly, possibly in concert with current producers, will quickly satisfy this market.

(5) Those utilities located near oil refineries in Toledo, Cleveland, and elsewhere should consider combining plant effluents for treatment in a Claus process for sulfur production using the SO_2 from the utility and H_2S from the refinery for the required feed streams.

(6) There may be a number of current special situations for individual Ohio utilities where production of a limited market product, such as gypsum or ammonium sulfate, might be preferable to all other options open to those utilities.

(7) Because of the relative costs of shipping sulfur or its derivatives compared with their low production costs, and because of the substantial excesses of by-product sulfur expected in most parts of the nation in the future, the market price for sulfur by-products from Ohio

utilities will probably drop precipitously as control technology becomes available during the next several years.

(8) Despite such a drop in price, the production of elemental sulfur may represent one of the most attractive products. Sulfur is relatively harmless from an environmental standpoint, and its disposal by selling even at depressed prices might obviate the costs of disposal of sludges produced by throw-away processes.

(9) In general, the production of any by-product which has even limited value in the open market place is preferable to production of by-products which have no value and require costs for disposal.

(10) In the long run, if sulfur emissions are fully controlled, there might develop a need for substantial sulfur additions as fertilizer to the soils in Ohio. This is not likely to occur, however, in the near future.

(11) The support of active research and development efforts to find new uses and expand the markets for sulfur by-products in order to minimize the decline in price structure of the by-products of Ohio's utilities is desirable.

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